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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

Submitted herewith is the final report on Contract NAS8-28058 with Athens State College. Chemical analysis of outgassing contaminants on spacecraft surfaces. Principal investigator Dr. Ronald C. McNutt.

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FINAL REPORT - CONTRACT NAS8-28058

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February 1977

I wish to thank the people who made significant contributions to this work, especially Dr. Gary Workman for his invaluable assistance, Dr. J. J. Cowan for his excellent work on the study of reflection grating anomalies, and Mr. David Jex for his cooperation and direction.

Dr. R. C. McNutt
Principal Investigator

I. Analysis of S-13 G Paint Extracts

Samples of S-13 G paint on aluminum were obtained from Space Sciences Laboratory. These samples are prepared for the vacuum distillation by scraping the S-13 G paint from the aluminum backing. They are then placed in the vacuum system and heated to approximately 200° C under about 10^{-5} torr. The distillate is collected in a small receiver immersed in liquid nitrogen. The S-13 G paint undergoes losses in weight of about 0.9% under these conditions, over a period of about ten hours.

We have found that at least two liquid phases of distillate (at room conditions) are produced. Tests have indicated the more dense phase to be water. The tests used so far on the distillate are gas chromatography and a standard spot test. The less dense distillate phase shows gas chromatographic peaks similar to that for a cyclohexane extract. This phase has general ultraviolet absorption similar to most outgassing contaminants we have examined. It is possible that some of the ultraviolet absorption arises from a functional group such as $>Si = o$, analogous to the carbonyl group $>C = o$.

The ultraviolet absorption spectra has been obtained on a sample of Coolanol-15, a siloxane refrigerant, in ethanol. The

spectrum is similar to that of spectrum from distillates of several paints and potting compounds.

Flourescence studies on an electret sample contaminated on Skylab have shown no fluorescence spectra either photographically or photometrically. There appeared to be a slight visually observed fluorescence. The results were not definitive due to the small quantity and the diffuse nature of the contaminant.

II. Experimental and Theoretical Studies of Reflection Grating Anamolies.

The general scope of this work has to do with the experimental and theoretical studies of reflection grating anomalies as affected by various dielectric (contaminant) coatings on the grating surface. These anomalies result from propagation of surface plasma wave (surface plasmons) on the metallic reflecting grating surface, and their properties are changed by predictable amounts depending on the thickness and type of dielectric layer.

The experimental work is concerned specifically with overcoating a 1200 linemm Al grating with thicknesses of As_2S_3 from 20 to 200 nm, stimulating oppositely directed surface plasma waves in these layers by intense 514.4 nm laser light, and as a result forming holograms on the surface. The interference maxima thus lie parallel to the surface and produce Lippman-Bragg scattering planes along the direction of motion of the surface waves. The holographic reconstruction of an image formed in this was found to have the following characteristics: (1) it is polarization dependent (only appears for p-polarized light) (2) it appears only when the surface wave is stimulated at the critical angle of incidence (3) both the critical angle and the width of the plasmon resonance vary with the thickness of the dielectric layer. The optimum layer thickness of As_2S_3 for

formation of holograms was found to be 50 nm. It was also discovered that bands of scattered light resulting from the decay of scattered surface plasmons appear above and below the plane of incidence. These bands can be used, it was found, to obtain information on such important parameters as plasma wave damping, dielectric thickness, and zone gap spacing in the plasma dispersion curve.

The theoretical work had to do with the development of a holographic formula for the surface wave energy density, assuming two waves propagate in opposite directions. The formula predi ts an enhancement of intensity over ordinary holographic methods by one to two orders of magnitude simply because of the use use of surface plasma waves.

Part of this work was reported on in a post-deadline paper presented at the Optical Society of America annual meeting at Rochester, N. Y., October 9 - 12, 1973, and the abstract will appear shortly in the Journal of the Optical Society. A complete paper which has been in preparation for some time on this and subsequent work is expected to be completed shortly and will soon be submitted to the Journal, Optics Communications. (See Appendix A)

III. Analysis of Rocket Effluents

Twenty-three samples of rocket effluents were obtained from SSL to be analyzed for iron, aluminum and organic material. The samples had been deposited from rocket exhaust onto small pieces of circular quartz.

The samples listed on Table 1 were obtained as alcohol slurries. The samples listed on Table 2 were received deposited on quartz, and were subsequently washed off the quartz surface to form a slurry in alcohol similar to the Table 1 samples.

The alcohol slurries were evaporated to dryness, leaving the original sample free of alcohol. These dry samples were then weighed. This weight was the basis for all percentage calculations. The dry samples in crucibles were placed in a muffle furnace for about 1-1/2 hours at 800 degrees Centigrade. This served to ignite and remove the organic material. The samples were then re-weighed and the weight loss determined. This weight loss is, of course, indicative of the amount of caronaceous material (hydrocarbons, etc.) present. The residue from ignition containing inorganic materials was then processed for the determination of iron and aluminum.

The analyses were carried out using standard colorimeteric techniques, with a Delta Scientific Model 260 colorimeter. (See

Appendix B) The results are summarized in Tables 1 and 2 that follow.

Two samples were selected to attempt to obtain some information on organic materials present. Sample number three was extracted with benzene. The extract was then evaporated to about one milliter volume. Ten microliters of this material were injected into a gas chromatograph. Figure 1 shows that at least five different components other than benzene were present in the sample. Sample number nine was extracted with cyclohexane. The extract was examined for ultraviolet absorption. Figure 2 shows the observed ultraviolet spectra. The cyclohexane was then evaporated from the sample and the infrared spectra obtained (Figure 3) on the residue. There appears to be only C-H vibrations and a definite indication of unsaturation. In summary the, the ultraviolet absorption indicated that some of the unsaturated components may be carbonyl compounds. The bulk of the organic material is probably various hydrocarbons with some indication of the presence of unsaturation.

Four samples of rocket effluents were received from Space Sciences Laboratory to be analyzed for aluminum. The analyses were carried out using the same method as with previous samples. One variation was made in the sample preparation. The samples

were wet-ashed, rather than being ignited in a muffle furnace. This technique has the advantage of not converting all the aluminum to difficultly dissolved Al_2O_3. (Table 3)

TABLE 3 - % Aluminum in Rocket Effluents

Sample	Wt. Total Sample	Wt. Dried Sample	Wt Aluminum	% Al in Dried Sample
003	70.60g	0.0092g	0.00004g	0.43%
005	69.60g	0.0056g	0.00033g	5.89%
006	73.45g	0.0157g	0.00151g	9.62%
010	69.80g	0.0139g	0.00152g	10.94%

We received six samples of rocket effluents from Space Sciences Laboratory to be analyzed to aluminum. The results are shown on Table 4.

TABLE 4 - % Aluminum in Rocket Effluents

Sample	Wt. Dried Sample	Wt Al./Sample	% Al./ Sample
003	0.0092g	3.9×10^{-5} g	0.42%
005	0.0056g	3.3×10^{-4} g	5.89%
006	0.0157g	1.5×10^{-3} g	9.56
010	0.0139g	1.5×10^{-3} g	10.79%
Filter S/N 001	0.0056g	0.4×10^{-3} g	7.14%
Filter S/N 002	0.0101g	0.5×10^{-3} g	4.95%

Table 1*

LIQUID SAMPLES

Bracket	Wt.Dried Sample	Wt.Ashed Sample	Ignition Wt. Loss	% Wt.Loss	Amount Fe	% Fe	Amount Al	%Al
2	1.7mg	1.7mg	0.0mg	0%	0.044mg	2.59%	0.050mg	2.94
3	48.4mg	47.7mg	0.7mg	1.45%	0.550mg	1.14%	0.398mg	0.82
5	3.5mg	2.9mg	0.6mg	17.14%	0.072mg	2.06%	0.098mg	2.80
6	1.5mg	1.2mg	0.3mg	20.00%	0.053mg	3.54%	0.043mg	2.87
7	1.0mg	0.8mg	0.2mg	20.00%	0.039mg	3.90%	0.024mg	2.40
8	20.7mg	19.8mg	0.9mg	4.35%	0.110mg	0.53%	0.600mg	2.90
9	NO WEIGHTS WERE TAKEN				0.188mg		0.630mg	
11	6.1mg	4.2mg	1.9mg	31.15%	0.107mg	1.75%	0.164mg	2.70
12	26.7mg	26.2mg	0.5mg	1.87%	0.351mg	1.32%	0.885mg	3.32
13	94.1mg	80.8mg	13.3mg	14.13%	1.045mg	1.11%	1.692mg	1.80
14	3.7 mg	2.9mg	0.8mg	21.62%	0.053mg	1.43%	0.087mg	2.35

*In general, reliability of these results are accurate to two significant figures.

Table 2*

SOLID SAMPLES

Bracket	Wt. Dried Sample	Wt. Ashed Sample	Ignition Wt. Loss	%Wt. Loss	Amount Fe	%Fe	Amount Al	%Al
2	5.1mg	2.4mg	2.7mg	53.94%	0.085mg	1.67%	0.100mg	1.96
4	16.9mg	16.2mg	0.7mg	4.14%	0.100mg	0.59%	0.275mg	1.63
5	1.6mg	1.6mg	0mg	0%	0.035mg	2.19%	0.025mg	1.56
6	2.9mg	2.8mg	0.1mg	3.45%	0.015mg	5.17%	0.130mg	4.48
7	0.4mg	0.1mg	0.3mg	75.00%	0.025mg	6.25%	0.038mg	9.50
11	4.6mg	3.8mg	0.8mg	1.74%	0.060mg	1.30%	0.245mg	5.33
12	7.1mg	5.8mg	1.3mg	18.31%	0.050mg	0.70%	0.195mg	2.75
13	4.4mg	3.6mg	0.8mg	18.18%	0.070mg	1.59%	0.140mg	3.18
14	2.2mg	0.6mg	1.6mg	72.73%	0.010mg	0.46%	0.048mg	2.18
15	1.2mg	1.0mg	0.2mg	16.67%	0.008mg	0.67%	0.036mg	3.00

*In general, reliability of these results are accurate to two significant figures.

Figure 1. G.L.C. scan of Benzene extract

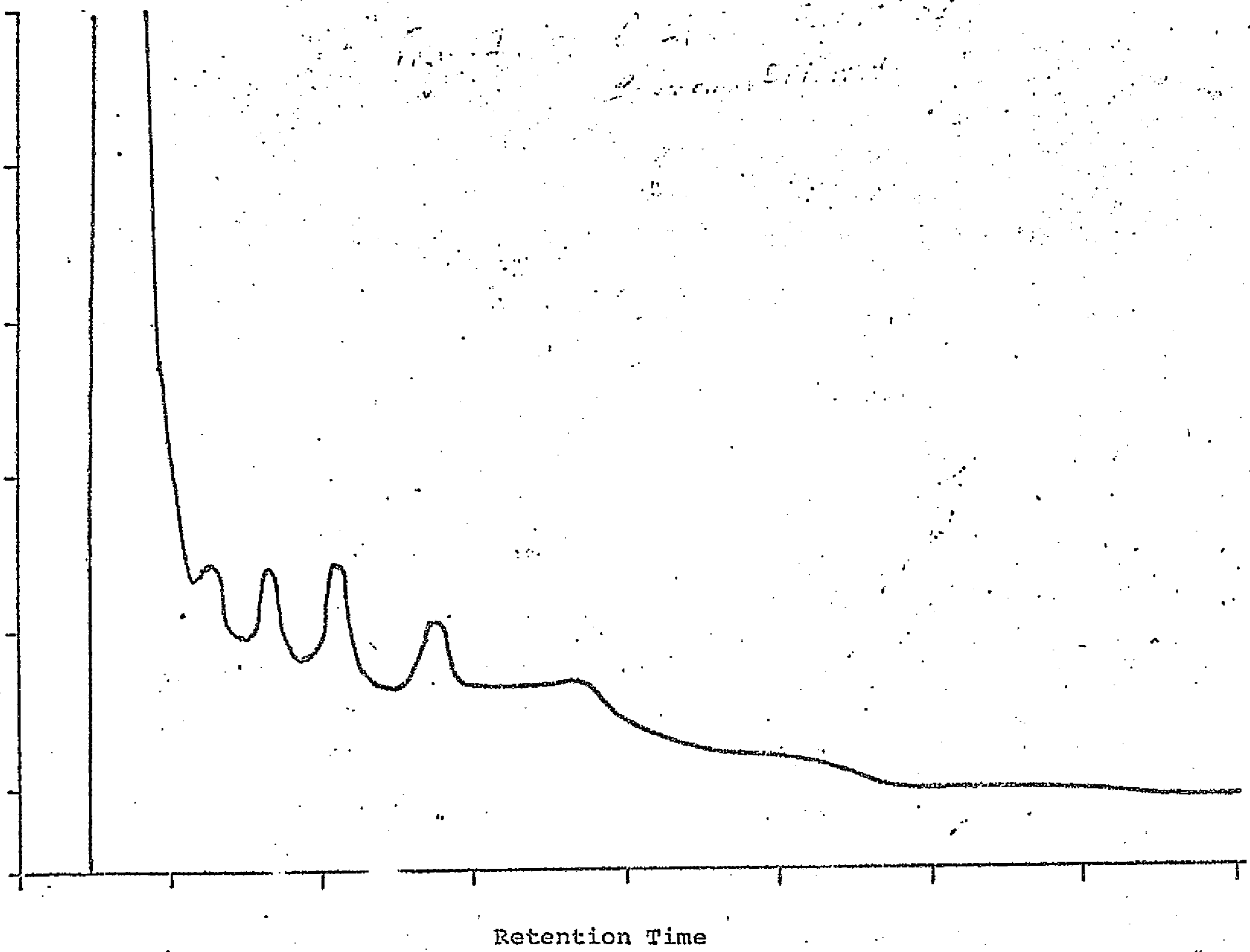


Fig. 2. Ultraviolet Spectra of cycl

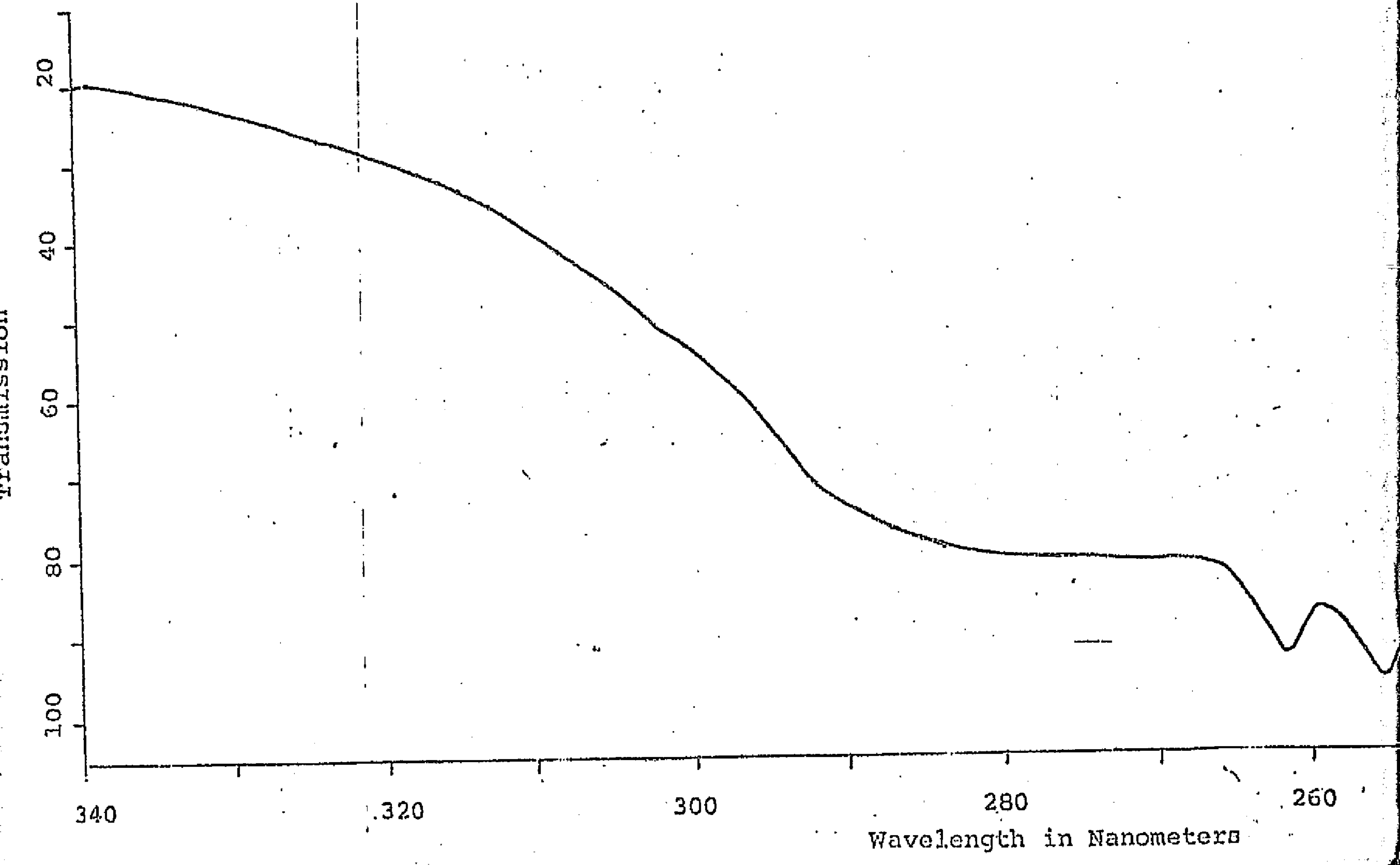
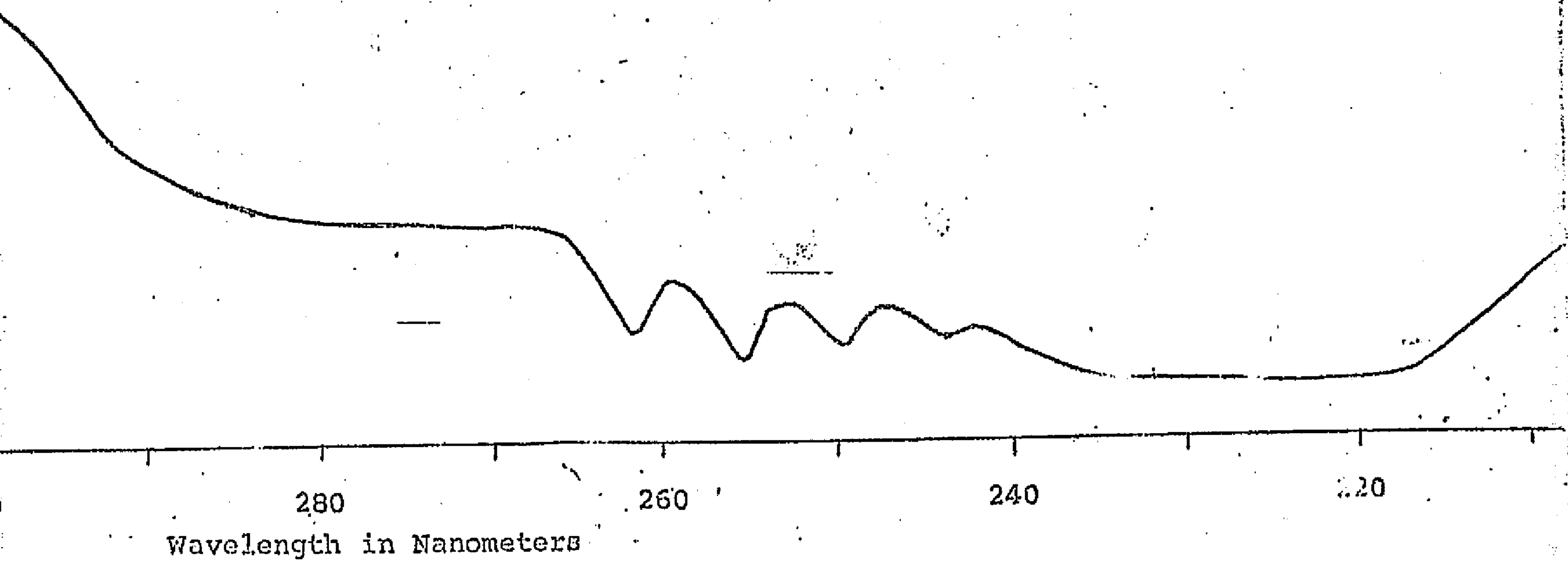


Fig. 2. Ultraviolet Spectra of cyclohexane extract



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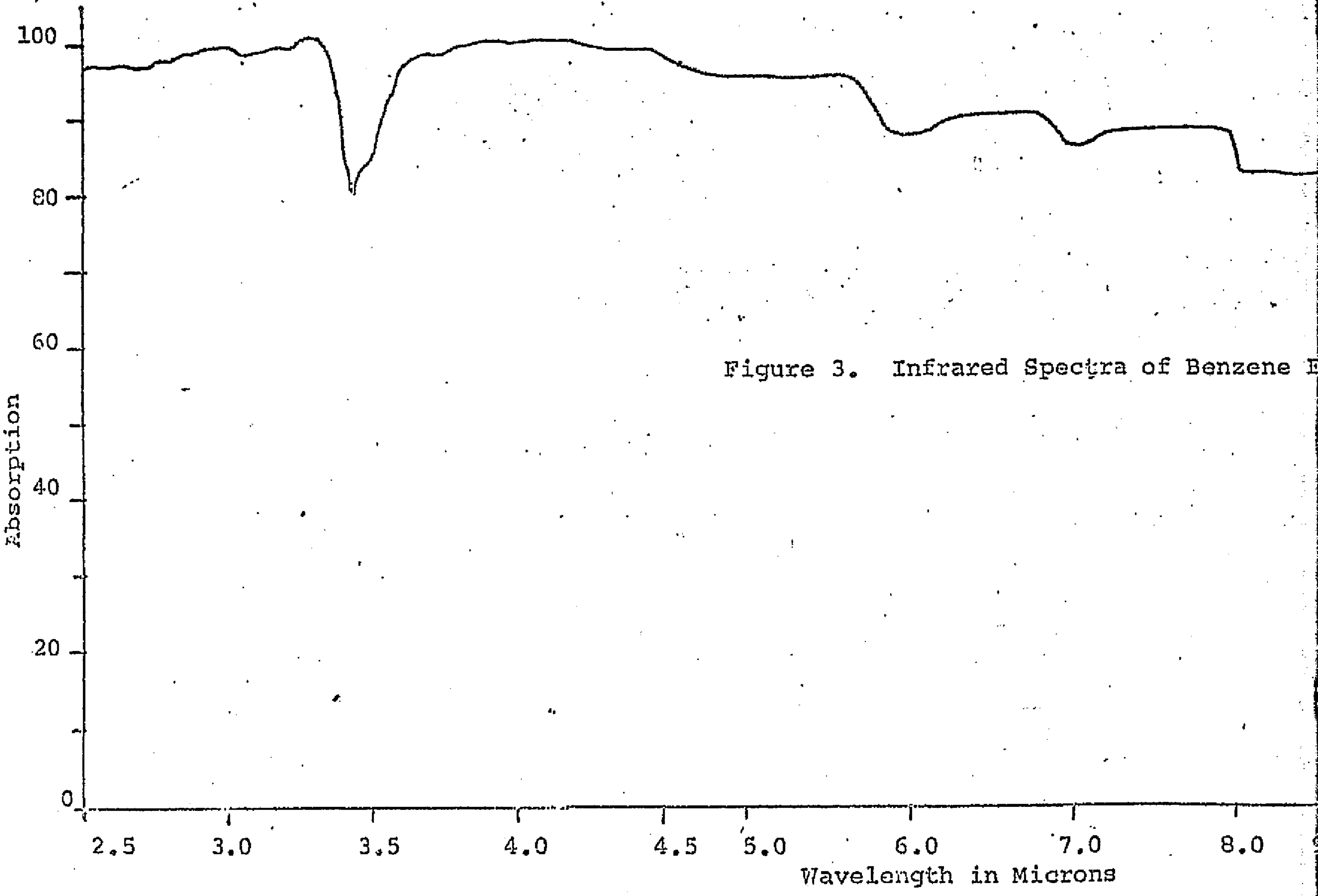

Figure 3. Infrared Spectra of Benzene E

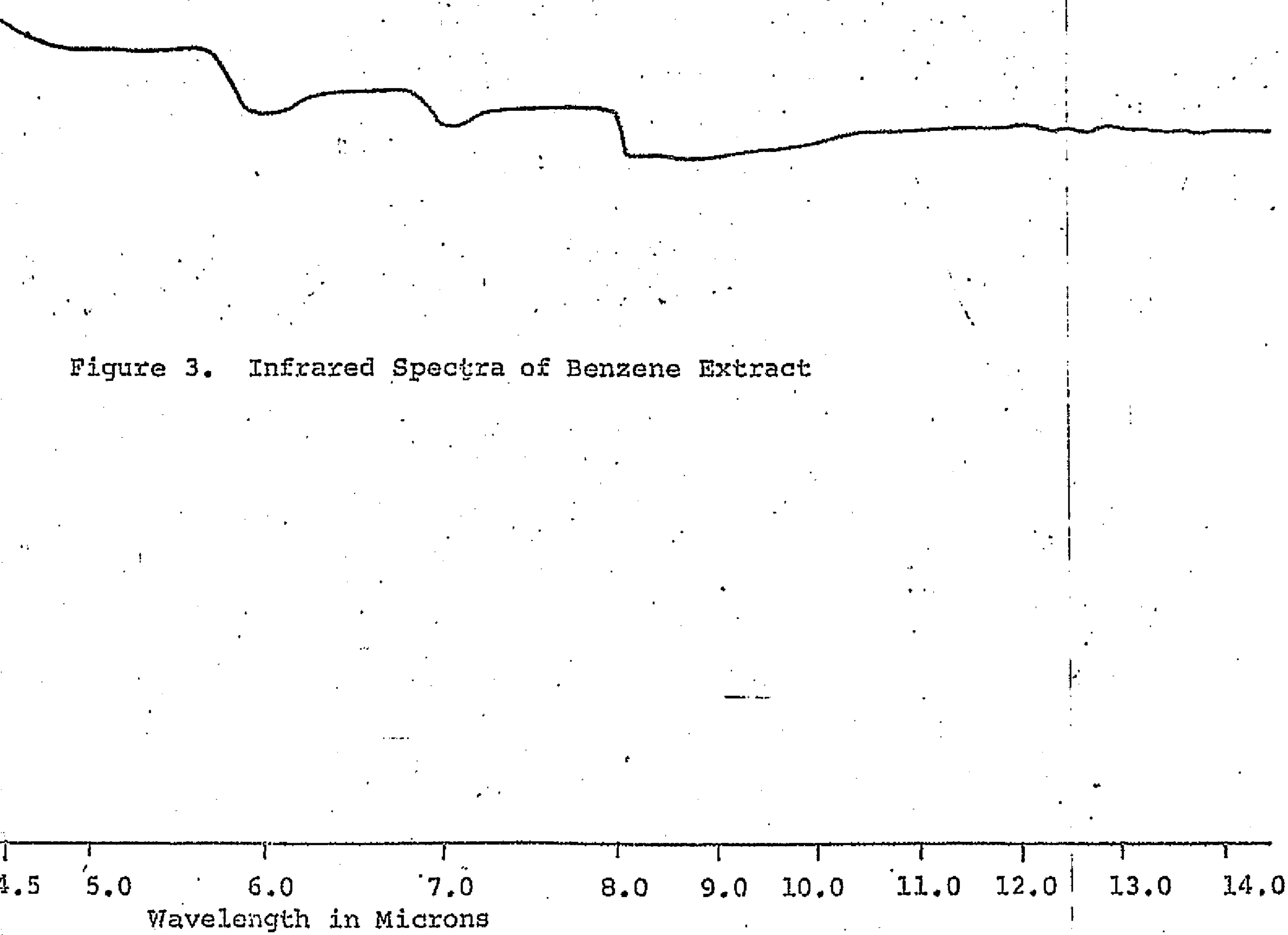

Figure 3. Infrared Spectra of Benzene Extract

We have analyzed six samples of rocket effluents from Space Sciences Laboratory for aluminum, iron, and weight loss on ignition. The results are summarized in Table 5. We should point out that some of these samples were extremely small. A standard automatic analytical balance, which we use, is accurate to $\pm$ 0.0001 g. One should observe the listed sample weigh s and consider the results accordingly.

Consider only the sample weight since the amounts of iron and aluminum were determined colorimetrically.

TABLE 4 - Analysis of Rocket Effluents

Sample	Dry Sample Weight (grams)	Sample Wt. (grams) After Ignition	% Wt Loss on Ignition	% Fe Colori-metri-cally	% Al Colori-metri-cally
17	0.0014	0.0013	7	71.4	21.4
19	0.0019	0.0018	5	31.6	7.9
26	0.0297	0.0248	16	14.5	1.0
35	0.0063	0.0032	49	12.7	3.2
39	0.0110	0.0079	28	17.3	5.5
45	0.0062	0.0027	56	6.3	2.6

We analyzed six samples of rocket effluents from Space Sciences Laboratory for aluminum, iron, and weight loss on ignition (See Table 6). We have obtained a slightly damaged Perkin-Elmer 303 Atomic Absorption Spectrophotometer. This will increase our capability for metal analysis. It should be pointed out that each

metal will require a specific cathode at a cost of about $150.00 each.

TABLE 6 - Analysis of Rocket Effluents

SAMPLE	% Fe	% Al	% Wt Loss on Ignition
Firing #4, Propellant #8, Dist. = 5" OS-12 Tuesday, April 23, 1974	5.7	2.5	47
Firing #10, Propellant #3, Dist. =5" OS-30 Wednesday, May 1, 1974	3.5	1.9	76
Firing #12, Propellant #12 Leading Sect. Windtek Filter #0009 OS 20 Thursday, May 2, 1974	8.1	3.0	81
Firing #19, Propellant #5, Dist. =5" Friday, May 10, 1974	6.7	3.6	78
Firing #19, Propellant #5, Dist. =11" Friday May 10, 1974	5.5	3.1	96*
Firing #19, Propellant #5, Dist. = 15" Friday, May 10, 1974	6.5	6.8	43

Percentages are based on dry sample weight.

* Essentially all the material in this sample was lost on ignition. Allowance for the apparent sum of more than 100% should be made in the % weight loss column due to weighing the very small amount of residue.

IV. Analysis of Skylab Window Scrapings

We received a small amount of material (for possible identification) from Space Sciences Laboratory that had been scraped from a Skylab window. We extracted part of this material with cychlohexane and obtained the ultraviolet spectrum of the extract (Figure 4). Another portion of the material was taken to the Stream Pollution Laboratory of the State Health Department of Tennessee in Nashville where equipment was available to prepare a micropellet with potassium bromide for the infrared spectrum. Mr. George E. Slate, of the State Laboratory, prepared the sample and obtained the spectrum (Figure 5). Figure 5 also shows the infrared spectra of Coolanol-15 and S-13 G base paint. It had been suggested that the material deposited on the Skylab window was derived from either S-13 G outgassing or from a Coolanol-15 leak. The ultraviolet spectra (Figure 5)was similar to that for Coolanol-15 dissolved in cyclohexane (Figure 6). However, the ultraviolet spectrum of cyclonexane extract from S-13 G paint (report this contract May 26, 1972) is also somewhat like that of the Skylab window scrapings. Consider Figure 5; the absorption peaks at 9.5 and 12.5 microns are of equal intensity in S-13 G. The 9.5 micron peak is much stronger than the 12.5 micron peak in Coolanol-15. The 12.5 micron peak is not equal to the

9.5 micron peak in the window scrapings. However, the peak at 12.5 microns does have significant intensity. The window scrapings and S-13 G both have a peak of significant intensity at 7.9 microns while no significant intensity is shown at 7.9 microns for the Coolanol-15. A peak is present at 7.25 microns in the window scrapings and Coolanol-15, it is very weak in the S-13 G, and appears to be shifted to 7.1 microns.

Dr. Joseph K. McDonald, spectroscopist with Athens College Math and Physics Department, has given the following as his opinion upon comparing the spectra: "When one considers the various spectra, then the best answer appears to be that the Skylab window scrapings are derived, at least in part, from both Coolanol-15 and S-13 G."

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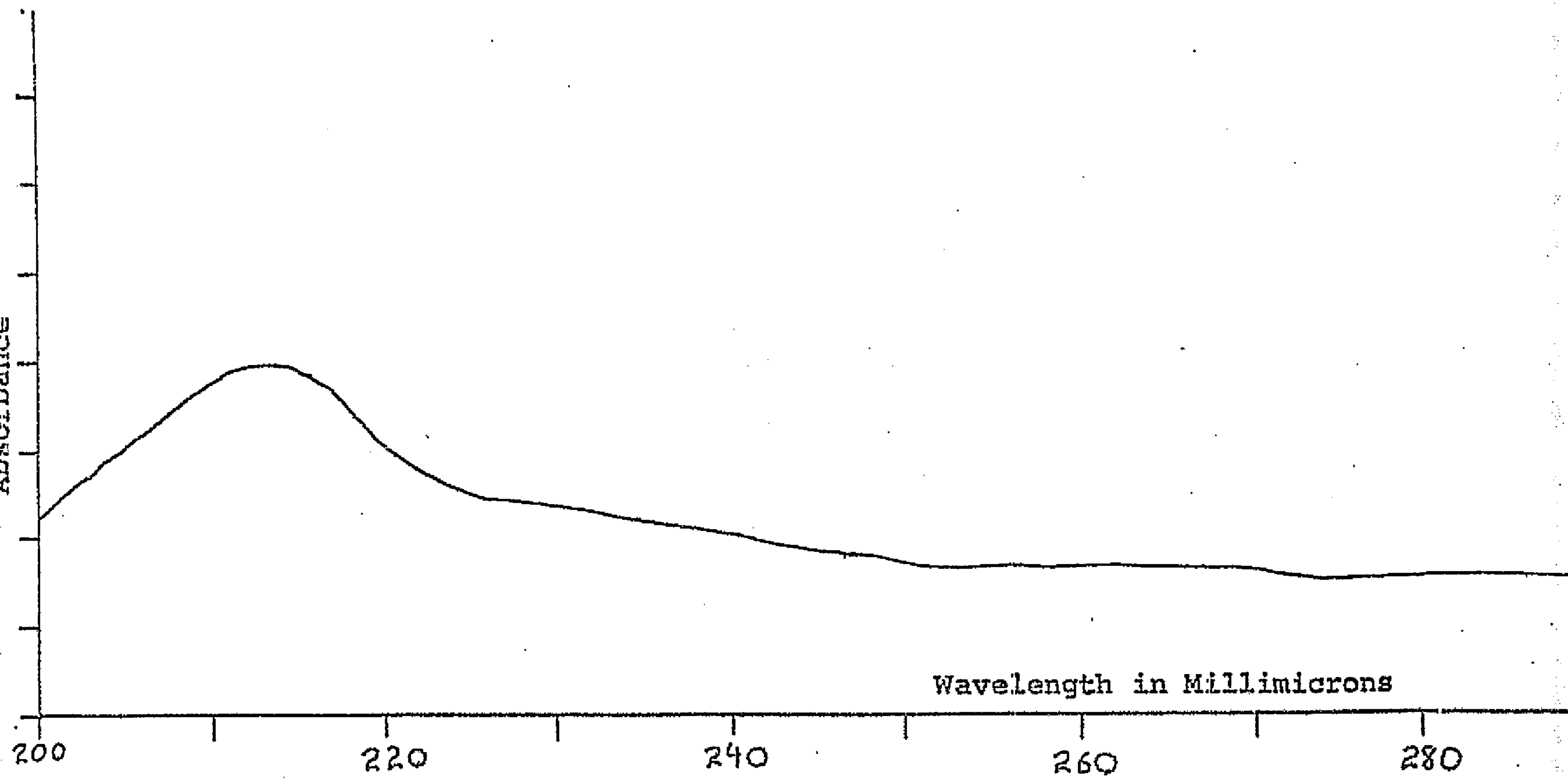
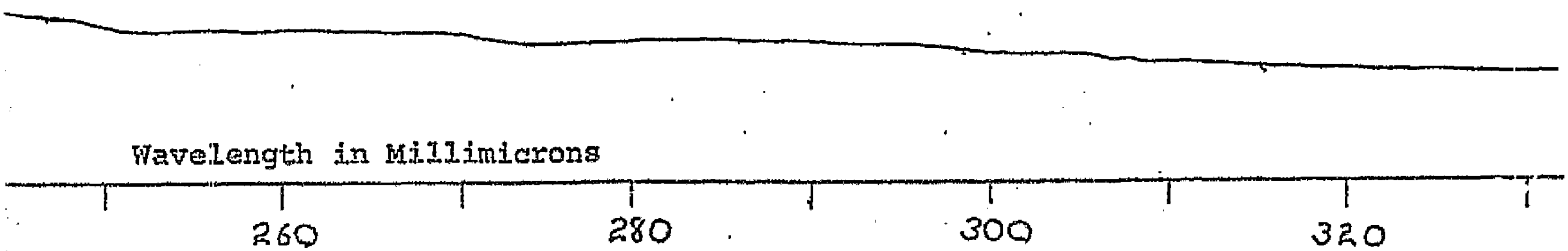


Fig. 4. Ultra-violet spectrum for cyclohexane extract of material scraped from



clohexane extract of material scraped from Skylab window.

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(18)

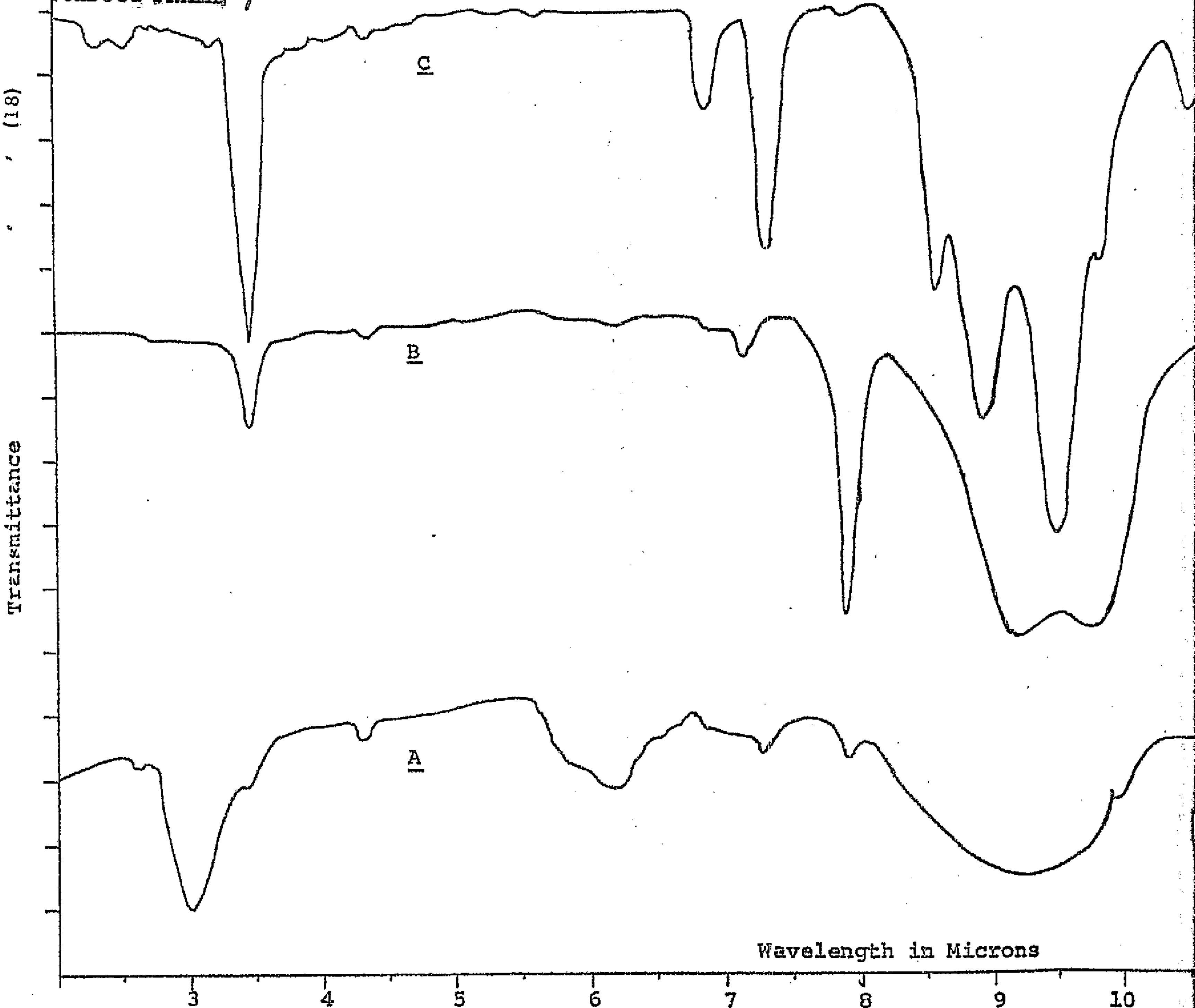
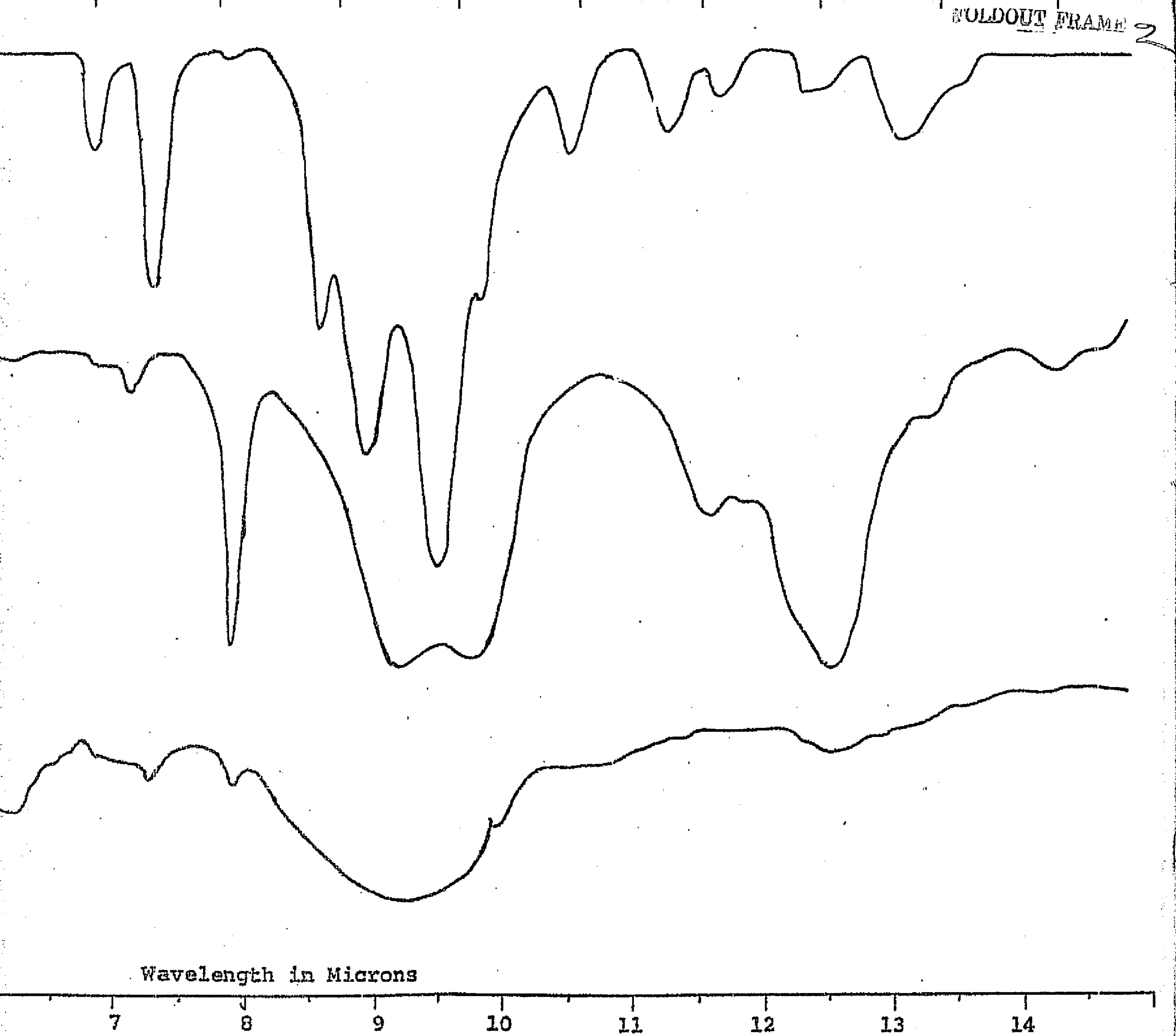


Fig. 5. A. Infrared Spectrum Skylab window scrapings B. S-13 G base paint C



window scrapings B. S-13 G base paint C. Coolanol-15

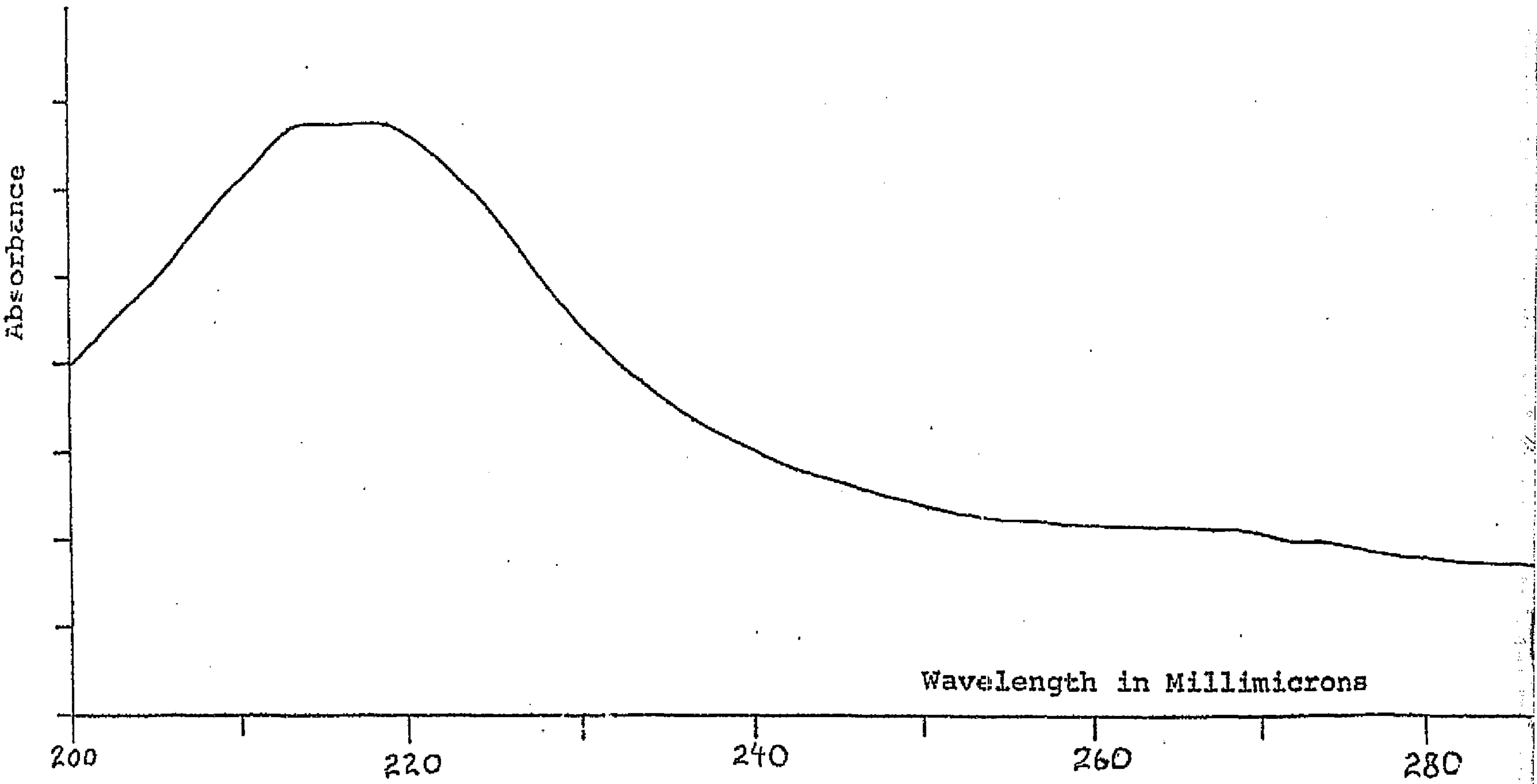
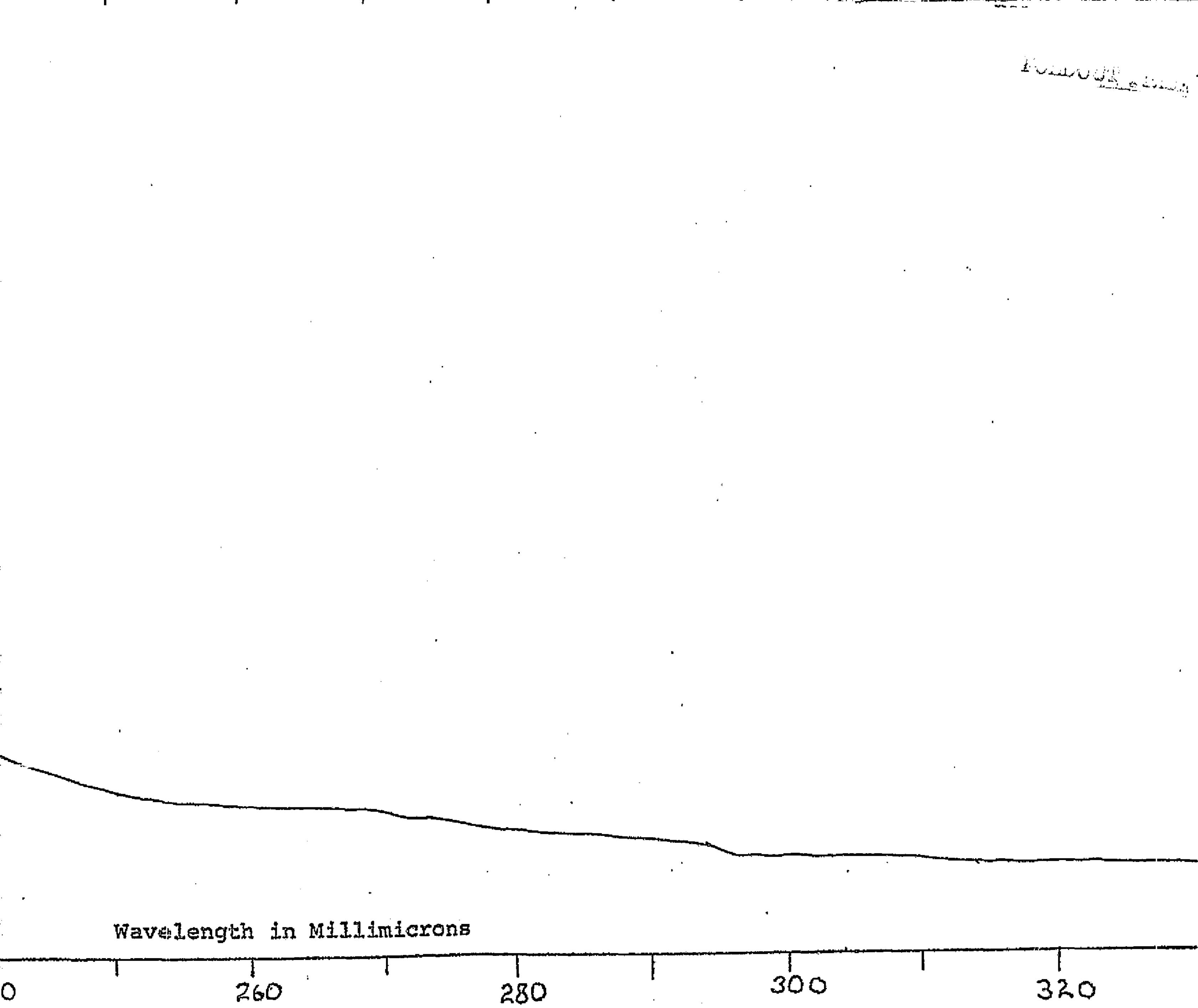


Fig. 6. Ultra-violet spectrum for Coolanol-15 in cyclohexane



anol-15 in cyclohexane

Table 7

"Radio Shack Semiconductor"

Compound	Temperature	Pressure (microns)	Indicator Response (milliamps)
Air	Room Temperature	1000	0.20
		500	0.22
		400	0.22
		300	0.23
		250	0.25
		200	0.29
Acetone	Room Temperature	1000	12.04
		500	12.00
		400	12.00
		300	11.97
		250	11.94
		200	11.94
	10° C	1000	12.00
		500	11.95
		400	11.95
		300	11.92
		250	11.90
		200	11.90
Ethyl Alcohol	Room Temperature	1000	12.10
		500	11.95
		400	11.90
		300	11.80
		250	11.65
		200	11.55
	10° C	1000	12.10
		500	12.00
		400	11.95
		300	11.80
Ethyl Ether	Room Temperature	1000	11.90
		500	11.85
		400	11.80
		300	11.75
	10° C	1000	11.95
		500	11.90
		400	11.90
		300	11.80

Table 7 (cont'd)

Compound	Temperature	Pressure (microns)	Indicator Response (milliamps)
Chloroform	Room Temperature	1000	10.95
		500	10.90
		400	10.80
		300	10.75
Hydrochloric Acid	Room Temperature	1000	10.15
		500	10.10
		400	10.05
		300	10.05
	10° C	1000	10.15
		500	10.10
		400	10.10
		300	10.05
Ethyl Alcohol (Tested again to see if HCl acid had damaged the detector)	Room Temperature	1000	12.05
		500	12.05
		400	12.00
		(These readings are approximately the same as the ones taken before, so it is assumed there is no damage)	
Cyclohexane	Room Temperature	1000	10.40
		900	10.10
Hexane	Room Temperature	1000	10.40
		900	10.30

V. Studies on a Gas Activated Semiconductor

We have collected data on the response of a gas activated semiconductor (a commercially available smoke detector "Radio Shack") to vapor from several volatile liquids. These include acetone, ethyl alcohol, ethyl ether, chloroform, hydrochloric acid, cyclohexane and hexane. The results are summarized in Table 7.

The detector did not appear to be very responsive to changes in temperature or pressure for a given compound. For the compounds tested, the organic compounds containing oxygen attained the highest response, approximately 13 milliamps. The other compounds showed a significantly lower value (10.0 - 10.9 milliamps). The results for water vapor were extremely erratic and nonreproducible (these results are not included in Table 7.). Ethyl alcohol was studied again after the other materials. The results were essentially the same as the earlier runs. It appears therefore that none of the materials, except hydrochloric acid, had any deleterious effect onthe semiconductor. The detector appeared to work well for some time after the HCl work, however, it later deteriorated. We have assumed this deterioration was due to HCl corrosion.

We have been flooding our vacuum system with the material being studi d and following the detector response as the system is pumped out. Our conclusion is that we have been following, not the detector response proper, but simply the rate of degassing the semi conductor which is extremely slow (three or four days). This accounts for the strange fact that the detector change was very slight over wide pressure ranges (from high pressure to low pressure pressure).

VI. Development of an HCl Detector

This work involves the coating of a TQCM (Thermal Quartz Crystal Microbalance) and QCM's with materials that react with HCl. Table 8 shows some preliminary results with triphenylamine.

We also investigated the reported reactivity of HCl (anhydrous and aqueous) with certain metals. Perfectly dry hydrogen chloride is relatively inert. For example, it reacts very slowly with zinc or magnesium. Aqueous HCl, hydrochloric acid, is a strong acid and will react with most metals except those with oxidation potentials less than hydrogen (i.e., copper, silver, and gold) with the liberation of H_2 gas and leaving the chloride salt of the metal usually with the metal in its lowest stable oxidation state.

In Table 9 we have listed the reaction of HCl (anhydrous, aqueous, or both) with several metals. A complete review of hydrogen halides is given in Comprehensive Inorganic Chemistry, Volume 2, 1280-1325 (1974) P.

HCl is not a powerful oxidizing agent and therefore will not react with the more inert metals except to furnish hydronium ion to enhance the corrosive power of other oxidants, such as oxygen.

A feasibility study was carried out at the Kennedy Space Flight Center on the use of amine coated QCM's for the detection of HCl from solid propellant rocket exhaust. Mr. David Jex MSFC-

SSL, Dr. Gary L. Workman, Athens College, and Dr. R. C. McNutt were present at the August 20 firing of the Viking II Mars Probe. Each had at least one amine coated QCM. Dr. Workman and Dr. McNutt were off-shore in boats. Mr. Jex was on shore. The exhaust cloud did not come over the boats; however, Mr. Jex was in the cloud path and was able to pick up a definite indication of HCl. The results of his findings are included in Mr. Jex's regular report at SSL. (NASA Technical Memorandum NASA TM X-64984).

We developed a vacuum technique for coating the QCM's with amine. It was decided to concentrate our efforts on the single crystal QCM for reasons of economy and simplicity.

A new technology report (MSFC-Form 3413) for a new type hydrogen chloride detector is included. (Appendix C)

Appendix D is a discussion of the general chemical and physical properties of amines.

Table 8

Response of an Amine Coated TQCM to HCl Vapor

The QCM was placed in a closed chamber and exposed to HCl vapors. After the crystal vibrations reached a maximum, the cover was removed and the HCl bottle closed.

Run 1

	Time(minutes)	Reading		Time (minutes)	Reading
	0	1857		39	2065
	1	1858		40	2059
	2	1860		41	2063
Cl	3	1859		42	2065
pened	4	1860		43	2068
ere→	5	1859		44	2070
	6	1874		45	2072
	7	1888		46	2075
	8	1894		47	2077
	9	1906		48	2079
	10	1919		49	2081
	11	1929		50	2084
	12	1939		52	2090
	13	1947		54	2094
	14	1953		56	2098
	15	1959		58	2102
	16	1963		60	2106
	17	1968		62	2109
	18	1972		64	2112
	19	1976		66	2116
	20	1982		68	2119
	21	1987		70	2124
	22	1993		80	2139
	23	1997		90	2154
	24	2002		95	2161
	25	2007		155	2238
	26	2012		156	2245
	27	2017		157	2246
	28	2022		158	2244
	29	2025		160	2243
	30	2028		170	2255
	31	2031		172	2252
	32	2034		174	2263
	33	2037		176	2262
	34	2041		178	2265
	35	2044		180	2260
	36	2047	HCl closed here;	185	2269
	37	2051	system opened →	190	2267
	38	2054		191	2209

Run I, continued

Time (minutes)	Reading
192	2199
193	2204
194	2201
196	2189
200	2145
202	2122
204	2105
206	2086
208	2080
210	2057
215	2014
220	1977
225	1952
230	1920
235	1899
240	1883
245	1872
260	1838
275	1802

Run II

The QCM was turned off for an extended period of time and when the second run was begun, the crystal readings were higher.

	Time (minutes)	Reading
	0	2967
	1	2967
	2	2964
	3	2964
	4	2962
HCl opened→	5	2960
	6	2973
	7	2994
	8	3000
	9	3004
	10	3009
	15	3044
	20	3090
	30	3158
	45	3240
	90	3460
	120	3519
	150	3529
	165	3534
HCl closed→	200	3552
	201	3543
	202	3535
	203	3526
	204	3528
	205	3513
	206	3515
	207	3507
	208	3502

Run III

The QCM was again turned off after Run II and left off for another extended period of time before Run III.

	Time (minutes)	Reading
	0	5199
	1	5212
	2	5210
	3	5207
	4	5207
HCl opened →	5	5204
	6	5212
	7	5222
	8	5238
	9	5256
	10	5271
	11	5298
	12	5318
	13	5339
	14	5363
	15	5382
	16	5402
	17	5416
	18	5431
	19	5442
	20	5454
	25	5503
	30	5542
	35	5573
	55	5672
	65	5703
	80	5737
	100	5781
	110	5800
	115	5830
HCl closed →	130	5854
	131	5824
	132	5800
	133	5794
	134	5783
	135	5777
	140	5752
	145	5747
	150	5718
	155	5701
	160	5683
	175	5664

Table 9

Reaction of HCl with Certain Metals

Metal	Reaction	Remarks
Li	$2Li + 2HCl \rightarrow 2LiCl + H_2$	Anhydrous or Aqueous
K	$2K + 2HCl \rightarrow 2KCl + H_2$	Anhydrous or Aqueous
Rb	$2Rb + 2HCl \rightarrow 2RbCl + H_2$	Anhydrous or Aqueous
Cs	$2Cs + 2HCl \rightarrow 2CsCl + H_2$	Anhydrous or Aqueous
Be	$Be + 2HCl \rightarrow BeCl_2 + H_2$	Anhydrous or Aqueous
Mg	$Mg + 2HCl \rightarrow MgCl_2 + H_2$	Anhydrous (slowly) or Aqueous
Ca	$Ca + 2HCl \rightarrow CaCl_2 + H_2$	Anhydrous or Aqueous
Ba	$Ba + 2HCl \rightarrow BaCl_2 + H_2$	Anhydrous or Aqueous
B	No Reaction	
Al	$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$	Aluminum Reacts slowly with HCl anhydrous at elevated temperatures. It is resistant to HCl aqueous.
Ga	$2Ga + 6HCl_{(aq)} \rightarrow 2GaCl_3 + 3H_2$	Gallium reacts very slowly with dilute aqueous HCl
In	$2In + 6HCl_{(aq)} \rightarrow 2InCl_3 + 3H_2$	Indium dissolves slowly in cold dilute HCl, more readily in hot concentrated HCl.
Tl	$HCl_{(aq)}$ reacts very weakly	HCl aqueous and HCl anhydrous react very slowly. Pb is very resistant to corrosion.
Si	No Reaction	
Pb	$Pb + 2HCl_{(aq)} \rightarrow PbCl_2 + H_2$	
As	No Reaction	
Sb	No Reaction	
Bi	No Reaction	
Ge	$Ge + 4HCl \rightarrow GeCl_4 + 2H_2$ $Ge + 3HCl \rightarrow GeHCl_3 + H_2$	HCl anhydrous reacts at elevated temperatures.
Sn	$Sn + HCl_{(aq)} \rightarrow SnCl_2$	Reacts slowly with dilute HCl. No reaction with HCl anhydrous.
Mn	$Mn + 2HCl \rightarrow MnCl_2 + H_2$	Anhydrous or Aqueous
Tc	No Reaction	
Fe	$Fe + 2HCl \rightarrow FeCl_2 + H_2$	Dilute HCl or HCl (anhydrous) at 450 degrees Centigrade.
Co	$Co + 2HCl \rightarrow CoCl_2 + H_2$	Dilute HCl
Ni	$Ni + 2HCl \rightarrow NiCl_2 + H_2$	HCl anhydrous at 500 degrees Cent.
Re	No Reaction	
Ru	No Reaction	
Os	No Reaction	
Ir	No Reaction, except in presence of strong oxidizing agent.	
Th	$Th + HCl_{(aq.con.)} \rightarrow ThO(X)H$	Where $X = OH^-$ or Cl^-
U	Dissolves readily in con.HCl	
Pu	$2Pu + 6HCl_{(anh)} \rightarrow 2PuCl_3 + 3H_2$	
Cu	Copper is attacked by moist HCl gas. Probable product $CuCl_2 \cdot 3Cu(OH)_2$ (Patina on Cu near the sea) Does not react with HCl anhydrous or HCl aqueous unless complexing or oxidizing agent is present.	

APPENDICES

APPENDIX A

Holography with Standing Surface Plasma Waves*

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It has been reported that surface plasma waves (surface plasmons), which are stimulated with p-polarized light on certain reflection gratings coated with photographic emulsion, can be used to form a hologram in the emulsion layer. In this case, ordinary object light interferes with the reference surface plasma wave. In experiments recently performed with a 1200line/mm, Al plane grating, it is demonstrated that holograms can also be formed in a 500 A^o evaporated overcoating layer of As_2S_3 using standing surface plasma waves, where both reference and object beams are surface waves but propagate in opposite directions. The image, formed with 5145 A^o laser light, is enhanced in reconstruction by the Lippman-Bragg effect, the scattering planes in this case being along the surface. Also the energy density of the plasma waves used here is increased over that for ordinary holography of an amount approximat y equal to the real part of the dielectric constant of the reflection layer (ε_1) for Al W at 5145 A^o). Also reported on is holo-

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graphy with object light alone, taking advantage of the beam splitting properties of the grating and using for a recording medium a 2500 A° layer of spin coated photoresist. Because the surface wave and the incident light that produce it are always coherent, application of this method to incoherent light holography is discussed. In all these experiments the image in reconstruction disappears completely if the polarization is changed from p to s or if the angle of incidence is changed to off-resonant condition.

HOLOGRAPHY WITH STANDING SURFACE PLASMA WAVES[☆]

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Holography with standing surface plasma waves, where both reference and object beams propagate in opposite directions, has been investigated using an Al reflection grating coated with evaporated As_2S_3 layers. The image, which appears only for p-polarization and at certain critical angles, is enhanced by the Lippman–Bragg effect and by an increase in intensity over ordinary holography approximately equal to $|\epsilon_1|$ for Al. Also considered is holography with object light alone in photoresist layers, using the beam-splitting properties of the grating.

When certain types of reflection gratings are illuminated with p-polarized light, it is possible, at certain critical angles of incidence, to excite surface plasma waves (surface plasmons) on the metal surface of the grating. The conditions for the formation of plasma waves, in addition to using p-polarized light, are that the metal have a value of the real part of the dielectric constant, ϵ_1, at the illuminating wavelength, less than -1, and that some means be provided at the metal surface to couple free space light with the slower propagating, evanescent surface wave. In this case the periodic grating structure provides the coupling mechanism and permits an easy resonant excitation of the surface waves [1]. The familiar Wood's anomalies have been related to these resonances [2]. If the grating is coated with a dielectric layer the plasmon resonances are broadened ans shifted to longer wavelengths, and the surface wave within the dielectric can be either evanescent or ordinary, depending on the thickness and optical properties of the dielectric [3]. It was previously reported [4] that if the dielectric is a high-resolution photographic emulsion, it is possible to produce holograms in this layer, using the interference of the ordinary light from the object with the surface plasma wave, here considered as the reference beam. After development and fixing of the emulsion layer, reconstruction could be carried out by re-exciting the surface wave. The primary disadvantage of this method was the difficulty in forming an even layer of emulsion on the surface and also the inherent difficulties associated with the shrinking of the emulsion in the development process.

We report here a continuation of these experiments with the difference that both object and reference light are surface plasma waves and the recording medium is a thin evaporated layer of dielectric. Furthermore, the plasma waves are excited such that they are propagating in opposite directions and thus an interference pattern of standing surface plasma waves is formed. We used a Bausch and Lomb 1200 line/mm, 1500 Å blaze, aluminum plane grating that was known to exhibit strong plasma resonances. The recording medium was a 500 Å layer of vacuum evaporated As_2S_3, a material that has been used with success previously in forming holograms with ordinary light [5]. The light source was the 5145 Å green line from an argon laser. The method of forming holograms was the same as that used previously; i.e., the beam is rotated by a half-wave plate so that it is polarized parallel to the plane of incidence, then is directed to a small area of the grating whose grooves run perpendicular to the plane of incidence. The direct laser beam is used here because of

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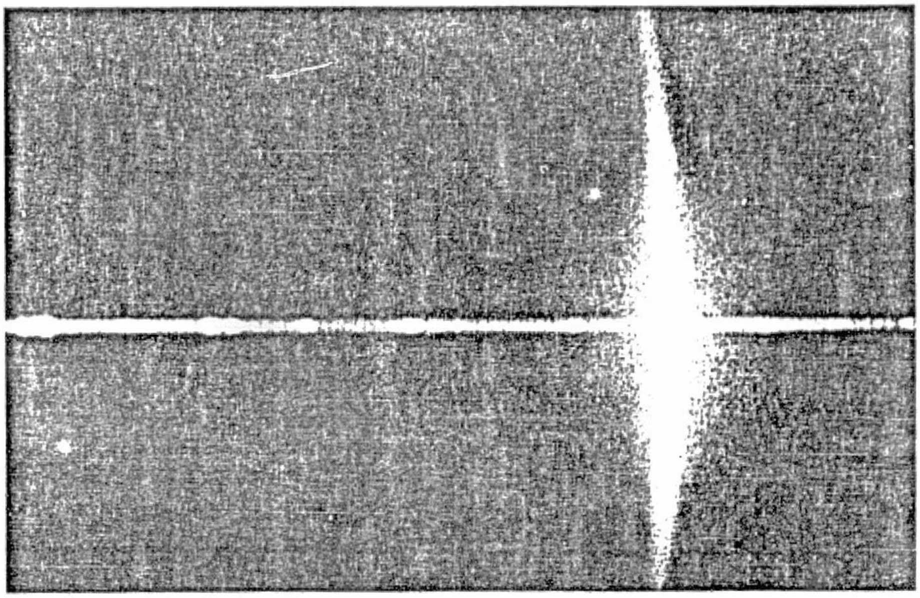

Fig. 1. Diffraction by grating under p-polarized light when surface wave is excited. Bright spot is reflected beam and horizontal band is plane of incidence containing grating ghost images. Bright vertical band is light resulting from decaying scattered surface plasmons propagating in same general direction on grating surface as primary beam. Dim vertical band is due to surface plasmons scattered in opposite direction on grating surface. When extended above the incidence plane these bands are found to intersect with a spacing characteristic of the band-gap spacing in the surface plasmon dispersion curve. Vertical bands disappear under s-polarization.

the high exposures required to form holograms in As_2S_3. The angle of incidence is then adjusted so that the first order on blaze diffracted beam runs off parallel to the surface; i.e., has a diffraction angle of 90°. A slight further rotation stimulates the surface wave, which is indicated when the off-blaze orders become dark. The degree to which these orders become dark is indicative of how much the surface wave resonance has been broadened. A further indication is narrow bands of light that appear along with the ordinary diffraction spectra but show up not only in the plane of incidence but also above and below this plane in directions roughly perpendicular to it (see fig. 1). These bands are due to surface plasmons formed by scattered light that themselves decay into light. They form at any angle of incidence but are especially intense at the on-resonant condition, the degree of intensity being indicative of the strength of the resonance. These bands are interesting in their own right as their shapes can be used to measure surface plasmon dispersion and band-gap spacing in the dispersion curve. This shall be discussed in detail in a subsequent publication.

It was found experimentally that the resonance was dampened considerably for dielectric thicknesses over 1000 Å and that thinner layers were necessary for the formation of holograms. A thickness of 500 Å was found to be a satisfactory value. Also, As_2S_3 at 5145 Å appears to be both a phase and an absorption recording material. This was evidenced by the fact that the resonance appeared to shift upon prolonged exposure. This was more pronounced at thicknesses from 500 to 1000 Å and above than for thicknesses less than 500 Å. In fact, the resonance was broad enough so that the shift at 500 Å thickness was not enough to move off resonance for any length of exposure.

The previous description applies for the general method of exciting surface plasma waves. A surface wave excited by the direct laser beam may be regarded as the reference beam. The object beam is excited in exactly the same way, except that one selects a different angle of incidence so that the resulting surface wave propagates in the opposite direction. A typical arrangement is shown in fig. 2 where the +3′ off blaze

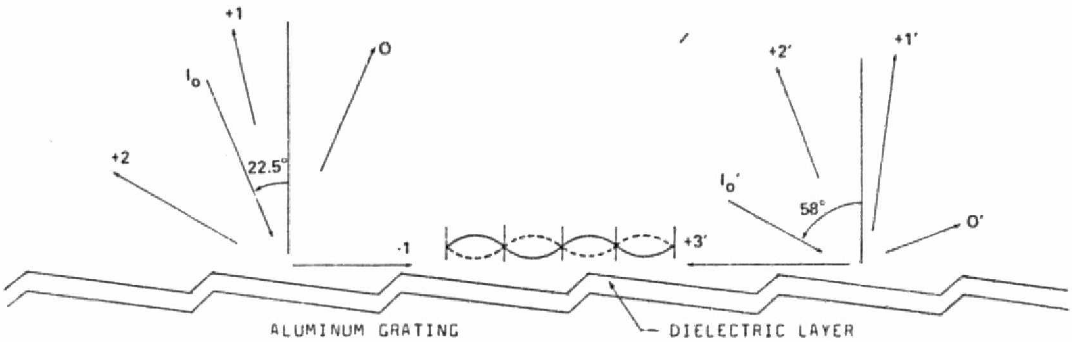

Fig. 2. Method of producing standing surface plasma waves. Beams I_0 and I_0' are respectively incident at 22.5° and 58° to give −1 and +3′ surface waves moving in opposite directions.

order produced by the object beam interferes with the −1 order produced by the reference beam. The two beams are, as usual, obtained from the same laser by means of a beam splitter. It is not necessary, however, that only the +3′ and −1 orders interfere. One could also use −1 and +2′ or +3 and −1′ or in fact any combination of oppositely directed surface waves, with the provision that the exciting object and reference beams, I_0' and I_0, both be on the same side of the grating normal. The reason for this is that the primary beams will themselves form interference fringes which could interfere with the surface wave fringes. If these beams strike the grating at relatively large incidence angles and in the same direction, their interference fringes will be predominantly parallel to the surface [6], and because of the thin layers used here their effect will be minimal. Since exposure alone and no development process is required for As_2S_3, it was sufficient simply to block out the object beam during exposure and see if an image formed in its place. Fig. 3 shows a hologram made in this manner, the image being of the +3′ beam as reconstructed by the −1 reference beam and deliberately recorded out of the incidence plane to distinguish it from the ordinary ghost images. The view in this figure is of the +1′ diffracted beam, but since the whole set of diffracted waves is reconstructed, there are similar images produced for 0′ and +2′. In a further experiment, the object beam was made distinctive from the reference beam by placing a small character (the letter 'x') in the object beam. The resulting hologram produced the image shown in fig. 4a. Fig. 4b is the same picture with polarization changed from p to s. For a beam power of about 700 mW and a spot about 16 mm^2, the exposure time for an image of reasonably good intensity ranged from 20 minutes to about 1 hour. This was for the −1, +3′ surface waves. For the +1′, −1 combination of surface waves, image formation occurred in a matter of a few minutes, but then faded away upon prolonged exposure, but this is believed due to the primary beams, as discussed above.

In reconstructing the object it was found that the bright image disappeared completely if (1) the angle of incidence were changed to the off resonant condition or (2) if the polarization were changed from p to s (see fig. 4b). In each of these cases one no longer ex-

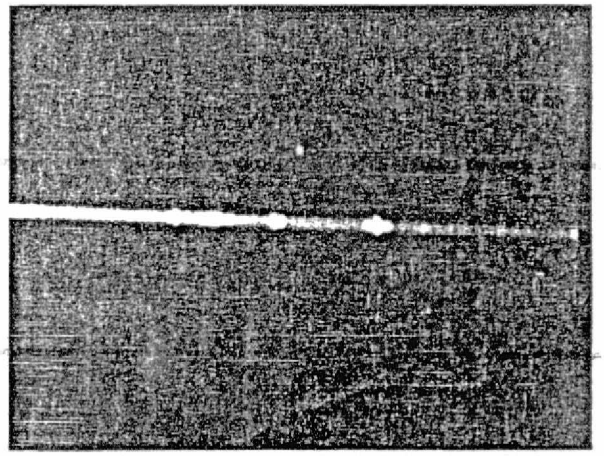

Fig. 3. Image of hologram produced by interference of −1 and +3′ surface waves. View is of +1′ diffraction as reconstructed by −1 surface wave reference beam.

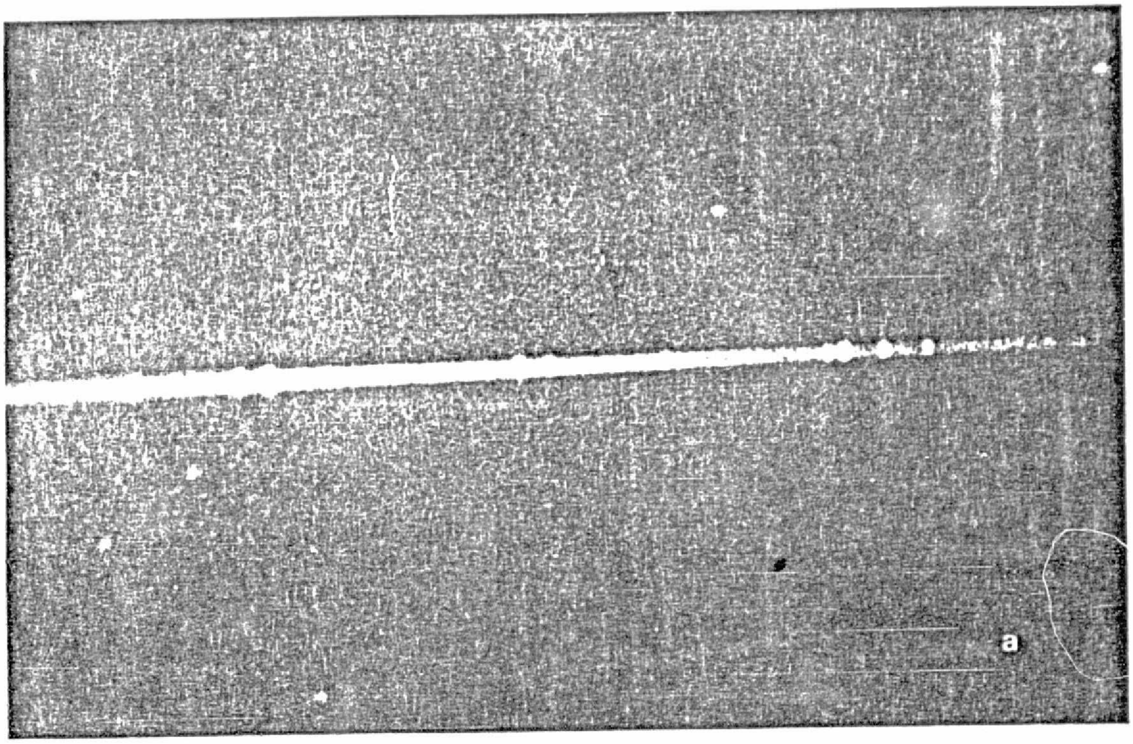

Fig. 4a. Image of hologram produced by interference of -1 and $+3'$ surface waves, where view is of $0'$ beam reconstructed by -1 surface wave and where the object beam I_0' contains the letter 'x'.

cites the surface wave and thus no image can be formed. Apparently no image is formed with the *ordinary* diffracted light because here the incident and reflected beams pass through a combined thickness of only about 0.1 μ. On the uncoated Al grating, on the other hand, the relaxation length of the exponentially decaying surface wave in its direction of motion (because of electronic and radiation damping) is about 20 μ‡. With the dielectric coating it is somewhat less than this. Thus, one expects the standing surface plasma wave interference pattern to form Lippman–Bragg scattering planes along the direction of wave motion much in the same way that these planes are formed for volume holograms, with the exception that in the former case they are along the surface of the recording medium instead of throughout the volume of the medium in the latter case. The brightness of the image is expected to be enhanced by the Lippman–Bragg effect, and this is indeed found to be true experimentally.

Another reason for enhancement of the surface wave image, that is, in relation to the required exposure time, may be related to the energy density of the surface waves involved. For example, at a metal–vacuum interface the field of a surface plasma wave propagating in the $+x$ direction is given by [8]

$$E_{s_1} = E_0\left(\hat{x} + \mathrm{i}\frac{k}{k_1}\,\hat{z}\right)\exp(\mathrm{i}kx - k_1 z - \mathrm{i}\omega t)$$

$$= E_0 \exp(\mathrm{i}kx)$$

and in the opposite direction by

$$E_{s_2} = E_0 \exp(-\mathrm{i}kx),$$

where E_0 = wave amplitude, k = surface plasmon wave number (in the x direction along the grating surface), $k_1 = \sqrt{k^2 - \omega^2/c^2}$ = wave number in the z-direction (perpendicular to surface), with ω and c being the frequency and free space speed of light, respectively. ϵ_1 is given in terms of k and k_1 by the relation $\epsilon_1 = -(k/k_1)^2$, which is the dispersion relation for the sur-

‡ This figure is obtained from the plasmon resonance half-widths. See ref. [7].

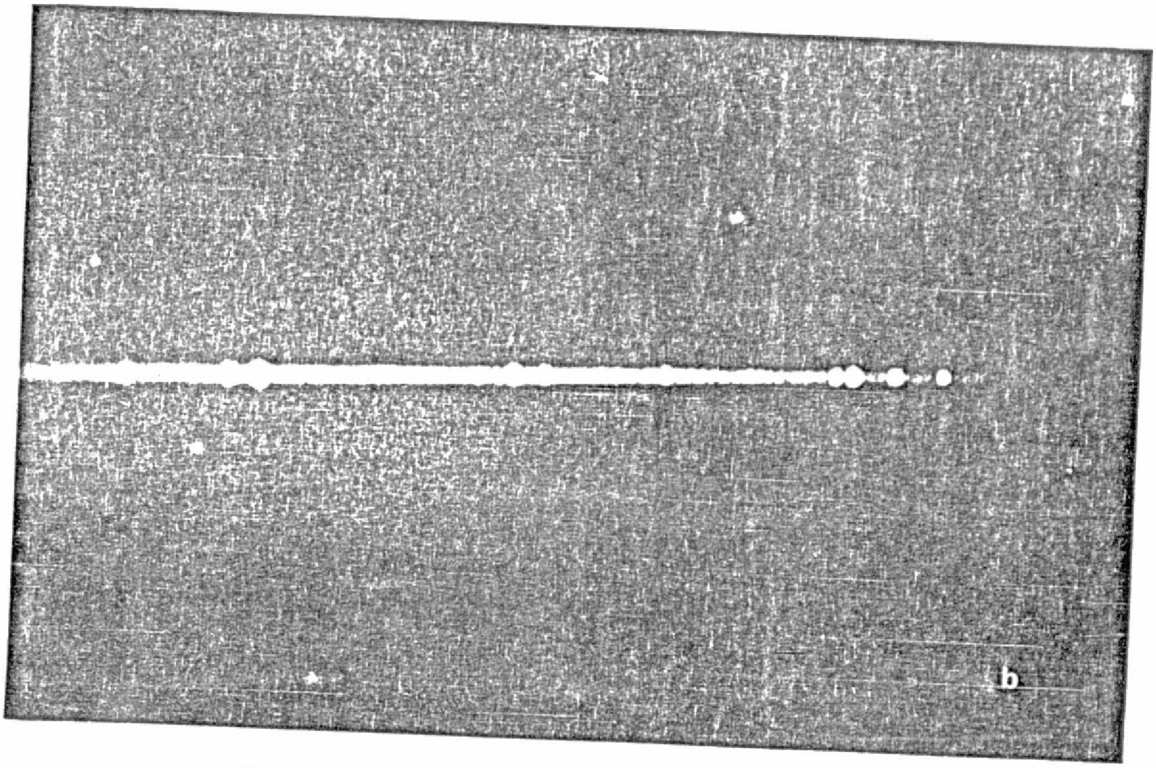

Fig. 4b. Same as fig. 4a, but with polarization changed from p to s.

face waves discussed here. Thus the intensity is

$$I = |E_{s_1}|^2 + |E_{s_2}|^2 + E_{s_1} \cdot E_{s_2}^* + E_{s_1}^* \cdot E_{s_2}$$

$$= 2E_0^2\left(1+\frac{k^2}{k_1^2}\right) \exp(-2k_1 z)$$

$$+ 2E_0^2\left(1+\frac{k^2}{k_1^2}\right) \cos 2kx \exp(-2k_1 z)$$

$$= E_0^2 \exp(-2k_1 z)(1+|\epsilon_1|)[2+2\cos 2kx].$$

The first term in brackets is the combined intensity of the two waves and the second term is due to interference. One sees that at the grating surface ($z = 0$) this equation has exactly the same form as that for ordinary wave holography, with the exception of the $1+|\epsilon_1|$ term. For Al at 5145 Å, $|\epsilon_1| \approx 40$ [9]. Thus, there is an enhancement in intensity between one and two orders of magnitude due to the fact that we are using surface plasma waves. While the presence of a thin dielectric layer would require more complicated equations*, its effect would not appreciably alter the qualitative conclusions reached here.

As a final consideration in using surface plasma waves in holography, there is the possibility of making holograms with incoherent light. If one illuminated the grating coated with the proper recording medium with light from some object at the critical angle, part of the light would go into the surface plasma wave and the rest would be either reflected or diffracted. The reflected beam is generally much more intense than any of the diffracted beams; however, because of the comments made in the preceeding paragraph, the surface wave intensity would become more important. The grating here would act as a beam splitter, and the average path length of about 20 μ of the surface wave is well within the coherence length of ther-

* For very thin layers, the surface wave within the dielectric would exhibit a sinesoidal dependence in the z-direction but is exponentially decaying in the metal and in the vacuum on either side. See refs. [1,3,7] for a detailed treatment. Also, we have assumed for simplicity that each surface wave has equal amplitude, but this is true only in special cases.

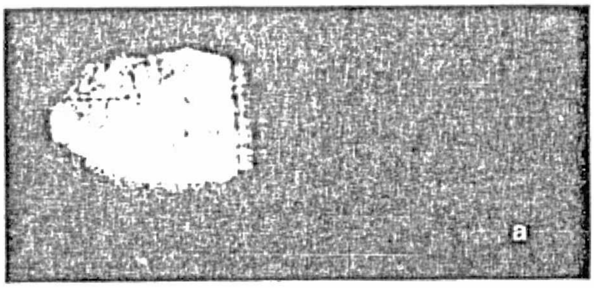

Fig. 5a. Hologram image produced by interference of I_0' and +3', where view is of +3' diffracted beam. Recording medium is 2500 Å spin-coated photoresist layer (Shipley AZ-1350B).

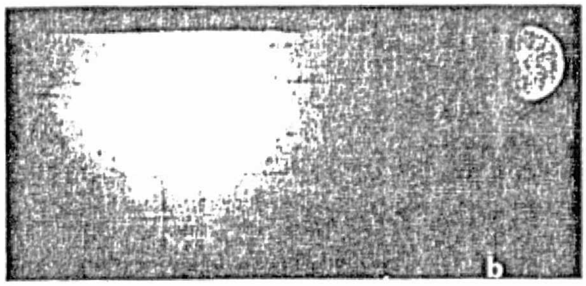

Fig. 5b. Same as fig. 5a, but with polarization changed from p to s.

mal light sources. The interference would be between the incident light and the surface wave resonance. If, in reconstruction, the grating were illuminated with a broad band (or white) light source at the critical angle, only the narrow resonances that had formed the hologram would be stimulated out of this spectrum. Thus, one should be able to reconstruct these holograms in white light in much the same manner as one reconstructs volume holograms with white light.

Preliminary attempts have been made to make holograms in this fashion with spin-coated layers of photoresist (Shipley AZ-1350B) but using coherent light. These layers, thicker than As_2S_3 at a value of about 2500 Å, were much less absorbing, as surface waves of reasonable intensity could still be produced. A hologram was made using the configuration of fig. 2 with the exception that only the object set of waves was excited. The interference in this case is between the incident object light I_0' and the surface wave +3'. Here, a greater dielectric thickness is desirable because the interference fringes are not exactly perpendicular to the surface but are oblique to it [6]. Also the resonance shift due to variations in photoresist thickness is much less apparent for a 2500 Å layer than it would be for thinner layers¶. Fig. 5 shows the results for p- and s-polarized light, where the object is a bar resolution chart and the source is the blue 4765 Å line of an argon laser. It is seen that the image appears only when the surface wave is stimulated at p-polarization. It was also found that when the angle of incidence was changed slightly to the off-resonant condition, the image disappeared. Although not so easily photographed, a clearly discernable image could be reconstructed in white light that exhibited the same polarization and angular dependence. Experiments are currently under way to make holograms with photoresist layers and incoherent light using for a source a blue line of a high-pressure Hg or Xe lamp, or by laser light passing through a moving diffuser.

¶ Small variations due to the development process in a dielectric thickness of a few thousand Å shift the dispersion curve less than if these same variations were imposed on a layer of only a few hundred Å.

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APPENDIX B

Test No. 260-31 -- Aluminum

The Reagents and Accessories required are as follows:

	R-183 Citric Acid Solution
	R-144 Aluminon Buffer Solution
	R-145 Potassium Cyanide, 1%, Stable Form
2	105-A Flasks, Erlenmeyer, 125 ml
1	103-A Cylinder, Graduated, 50 ml
2	126-A Pipettes, Mohr Measuring, 1 ml
1	109-A Pipette, Dropping, 1 ml

1. Using a No. 103-A 50 ml Graduated Cylinder, measure 50 ml of sample into a No. 105-A 125 ml Erlenmeyer Flask.

2. Rinse the cylinder with aluminum-free distilled water, and prepare a reagent blank by measuring 50 ml of aluminum-free distilled water into a second 125 ml Erlenmeyer flask. See Note B.

3. Using the 1 ml Dropping pipette, add to each flask 1 ml of freshly prepared No. R-145 Potassium Cyanide, 1%, and mix. Caution! POISON. See Note A for preparation and stability of solution.

4. Add to each flask 1 ml of No. R-144 Aluminon Buffer Solution and mix. Note the time and let stand for exactly 30 minutes.

5. Turn on the instrument and rotate the filter selector to No. 250.

6. Fill one No. 260-T Square 26 mm Test Cell with the reagent blank. Fill a second test cell with the treated sample.

7. Insert the test cell contai ing the blank into the Analyzer, making certain that one of the frosted sides faces to the front. Adjust the meter needle to a reading of 100.

8. Replace the blank with the test cell containing the treated sample and read the meter.

9. Refer to the graph for Aluminum to convert the meter reading to parts per million Aluminum (Al). The Model 260 Water Analyzer is calibrated from 0 - 1.0 parts per million Aluminum. If necessary expand the range as described in the introduction.

NOTE A - To prepare Potassium Cyanide, 1%, add 100ml of distilled water to the 4 ounce bottle, containing the 1 gm. of Potassium Cyanide. Replace the cap and shake until dissolved. Record the date of preparation on the bottle label and discard the unused portion after two weeks.

WARNING - This solution is poisonous, use the No. 109-A ml Dropping Pipette for measuring.

NOTE B - If the sample is colored or turbid, prepare a blank by using 50 ml of sample instead of distilled water in the procedure given above, except in Step 3 - omit the No. R-145 Potassium Cyanide, 1% and substitute 1 ml of No. R-183 Citric Acid Solution. Substitute this sample blank for the reagent blank in Step 6. If the sample blank is so highly colored or turbid that the instrument cannot be set to 100 then use distilled water as a blank in Step 7 and read both the sample blank and the unknown. Convert the meter readings to ppm and subtract the value (in ppm) of the sample blank from the value (in ppm) of the unknown. The difference is the true concentration of unknown in the sample.

Test No. 260-14 -- Iron

The Reagents and Accessories required are as follows:

	R-101	Ammonium Acetate Buffer
	R-39	Hydrochloric Acid, Concentrated
	R-100	Hydroxylamine Reagent
	R-63	Iron Reagent Powder
	R-102	Phenanthroline, 0.1%
2	103-A	Cylinder, Graduated, 50 ml
2	105-A	Flask, Erlenmeyer, 125 ml
2	107-A	Flask, Volumetric, 50 ml
2	110-A	Pipette, Mohr Measuring, 5 ml in 1/10 ml
	112-A	Scoop

Procedure A - Rapid dry powder method for Dissolved Iron, in waters which are FREE OF ORGANIC OR OTHER INTERFERENCES.

1. Measure, with a No. 103-A 50 ml graduated cylinder, 25 ml of filtered sample, and pour into a No. 105-A 125 ml Erlenmeyer flask.

2. Add 1 No. 112-A Scoop (approx. 380 mg) of No. R-63 Iron Reagent Powder, and mix. Let stand for five minutes.

3. Turn on the Analyzer and rotate filter selector to No. 520.

4. Fill one No. 260-T Square 26 mm Test Cell with untreated filtered sample, for use as a blank. Fill a second test cell with the treated sample.

5. Insert the test cell containing the blank into the Analyzer, making certain that one of the frosted sides faces to the front. Adjust the meter needle to 100. See Note B.

6. Replace the blank with the test cell containing the treated sample, and read the meter.

7. Refer to the graph for Iron to convert the meter reading to ppm Iron (Fe).

Procedure B - This is based on the standard A.P.H.A. method, 12th edition, using Phenanthroline, where the sample is TREATED TO REMOVE INTERFERING SUBSTANCES. The same calibration graph is used for both procedures.

1. (a) For total Iron, mix the sample thoroughly and measure 50 ml of mixed sample into a 125 ml Erlenmeyer flask.
   (b) For Dissolved Iron, allow the sample to settle, decant the supernatant, and filter, discarding the first 25 ml of filtrate. Measure 50 ml into a 125 ml Erlenmeyer flask.

2. Simultaneously prepare a reagent blank by adding 50 ml of distilled water to a second 125 ml Erlenmeyer flask. See Note C.

3. To each flask, add 2 ml of No. R-39 Hydrochloric Acid, Concentrated, and 1 ml of No. R-100 Hydroxylamine Reagent.

4. Heat both flasks to boiling on a hot plate and reduce the volume to approximately 20 ml. (See Note A)

5. Cool to room temperature and transfer each to No. 107-A 50 ml Volumetric Flasks.

6. To each, add 10 ml of No. R-101 Ammonium Acetate Buffer and 3 ml of No. R-102 Phenanthroline, 0.1%.

7. Dilute each flask to volume with distilled water, and mix. Let stand for five minutes.

8. Continue as directed in Procedure A, beginning with Step 3.

9. The Model 260 Water Analyzer is calibrated from 0 to 5 ppm Iron (Fe). If necessary expand range as described in the Introduction. The results are reported in ppm Iron, either Total or Dissolved. Total Iron is obtained with mixed, unfiltered sample. Use of filtered sample gives results in terms of Dissolved Iron only.

NOTE A - If the sample contains much color or organic matter, evaporate a 50 ml sample, gently ash the residue, and redissolve in 2 ml of No. R-39 Hydrochloric Acid, Concentrated. Add 1 ml of No. R-100 Hydroxylamine Reagent, and 5 ml of distilled water. Proceed with Step 5.

NOTE B - If the sample blank is so highly colored or turbid that the instrument cannot be set to 100 then use distilled water as a blank in Step 5 and read both the sample blank and the unknown. Convert the meter readings to ppm and subtract the value (in ppm) of the sample blank from the value (in ppm) of the unknown. The difference is the true concentration of unknown in the sample.

NOTE C- If the sample is colored or turbid prepare a blank by using 50 ml of sample instead of distilled water in the procedure given above, substitute distilled water for reagents in Step 6. Use the sample blank instead of the reagent blank in Step 4.

If the sample blank is so highly colored or turbid that the instrument cannot be set to 100 then use distilled water as a blank in Step 5 and read both the sample blank and the unknown. Convert the meter readings to ppm and subtract the value in (ppm) of the sample blank from the value (in ppm) of the unknown. The difference is the true concentration of unknown in the sample.

NOTE D - Estimating ferrous and ferric iron -- the procedures given above convert all the iron in the sample to the ferrous (Fe^{++}) form before the color reaction with Phenanthroline. The quantity of ferric iron (Fe^{++})present may be estimated by adding 1 ml No. R-39 Hydrochloric Acid, Concentrated, to 50 ml of sample in an Erlenmeyer Flask, mixing and proceeding at once to Step 6 in Procedure B. Continue without delay to Step 8 of procedure B. Convert the reading obtained to ppm Fe from the graph, and multiply by 1.2. The value obtained will be close to the quantity of ferrous iron originally present. Subtracting this from the total iron (determined as described in Procedure B) will give the quantity of iron originally present in the ferric form.

MARSHALL SPACE FLIGHT CENTER/NASA

NEW TECHNOLOGY REPORT

NT CONTROL NO. (Official use only):

INSTRUCTIONS

See Documentation Guidelines for NT Reporting for NASA Form 666.A (NHB 2170.3 April 1969)

1. TITLE:

A New Type of Hydrogen Chloride Detector

2. INNOVATOR (S) (Name and Social Security No.):

Gary L. Workman [redacted]

3. EMPLOYER (Organization and division):

Athens College
Science Division

4. ADDRESS (Place of performance):

Athens, Alabama 35611

5. NASA PRIME CONTRACT NO.:

NAS8-28058

6. CONTRACTOR DISCLOSURE NO.:

SECTION IV - ADDITIONAL DOCUMENTATION (Include or list below any pertinent documentation which aids in the understanding or application of the new technology. IF NOT TOO BULKY OR DIFFICULT TO REPRODUCE, INCLUDE COPIES WITH THIS REPORT. For those references or additional documentation available but NOT included in this report (due to their being nonessential to a basic understanding of the new technology and which may be costly to reproduce or handle) complete item A, below):

A. AVAILABLE DOCUMENTS (Check and complete)						
		1. PAPERS, ARTICLES		4. ASSEMBLY/MFG. DRAWINGS		7. TEST DATA
		2. CONTRACTOR REPORTS		5. PARTS OR INGRED. LIST		8. ASSEMBLY/MFG. PROCED.
		3. ENGINEERING SPECS.		6. OPERATING MANUALS		9. COMPUTER TAPES/CARDS
	10. OTHER (Specify):					

B. INDICATE THE DATES OR THE APPROXIMATE TIME PERIOD DURING WHICH THIS TECHNOLOGY WAS DEVELOPED (i.e., conceived, constructed, tested, etc.):

Conceived 1-75
Developed and demonstrated 7-1-75

C. LIST THE FIRST PUBLICATION OR PUBLIC DISCLOSURE OF THE NEW TECHNOLOGY, AND DATES:

None as yet

D. LIST THE DATES AND ANY PARTICULARLY PERTINENT PAGE NUMBERS OF OTHER PUBLICATIONS WHICH ARE AVAILABLE BUT NOT ATTACHED:

None

E. DEGREE OF TECHNOLOGICAL SIGNIFICANCE (Check in your best judgement the statement which best expresses the degree of technological significance of this technology):

[ ] 1. MODIFICATION TO EXISTING TECHNOLOGY [X] 2. SUBSTANTIAL ADVANCE IN THE ART [ ] 3. MAJOR BREAKTHROUGH

COMMENTS:

NT CONTROL NO. ______________

SECTION I - DESCRIPTION OF THE PROBLEM THAT MOTIVATED THE TECHNOLOGY DEVELOPMENT (Enter A. - General Description of Problem Objective; B. - Key or Unique Problem Chocteristics; C. - Past History/Prior Techniques; D. - Limitations of Prior Techniques):

A. Hydrogen chloride gas is a noxious product of industrial chlorine processes and solid rocket propellants. Therefore, an inexpensive, portable, and sensitive hydrogen chloride monitor is needed. The development here was initiated due to the requirement that environmental conditions around rocket launch sites have to be maintained.

B. Unique problems exist in measuring HCl. Most acids will reach similarly, as well as some redox type reactions. Therefore to come up with a specific detector is a challenge.

C. Prior techniques include acid-base coulometric titration, catalyzed chemiluminescence, and mass spectrometric. The first two are not specific and the last technique has proven to be too expensive. The catalyzed chemiluminescence is sensitive, but has limited range and specificity. For instance, SO_2 would be a primary interference in either of the first two techniques.

SECTION II – TECHNICALLY COMPLETE AND EASILY UNDERSTANDABLE DESCRIPTION OF NEW TECHNOLOGY THAT WAS DEVELOPED TO SOLVE THE PROBLEM OR MEET THE OBJECTIVE (Enter as appropriate A.-Specific description of item; B.-State of development; C.-Operation as a unit; D.-Functional operation; E.-Supportive theory; F.-Engineering specifications; G.-Peripheral equipment; H.-Drawings, graphs, etc.; I.-Parts or ingredients lists; and J.-Maintenance, reliability, safety factors)

A. A hydrogen chloride detector has been developed using the chemical reaction:

$$R_3N + HCl \rightarrow R_3NH^+Cl^-$$

where R_3 represents an organic compound attached to the amine nitrogen. The reaction is monitored by any microbalance capable of measuring extremely small mass differences in real time. The sensitivity of the detector then is determined by the sensitivity of the microbalance used. The ultimate range of detectibility is likewise determined by the instrumental characteristics of the microbalance used and the total number of amine molecules which can be deposited on the microbalance and the total number of nitrogens per molecule.

B. The technique has been demonstrated using a quartz crystal microbalance as the mass indicator and triphenylamine for the coating. With a sensitivity of 10^{-9} gms/frequency, the detector is capable of responding to $\sim 10^{-8}$ grams of hydrogen chloride or 2.5×10^{14} molecules. Since this detector operates as an accumulative collector, integration by time, enables very low concentrations (less than parts-per-million) to be attainable. The coating most often used for development has been triphenylamine. Chemisoption or a specific chemical reaction best describes the process overall.

NT CONTROL NO.

SECTION II (Continued):

C. The lone nitrogen pair of the compound easily (and specifically) binds polar HCl at each site. Less polar species and larger molecules are less likely to react if tertiary and secondary type amines are used. Any mass detector, upon which amine coating can be deposited is suitable to provide HCl detection.

D. Peripheral equipment- mass detector, and its associated peripherals. Coater to deposit amine coating.

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SECTION II (Continued):

SECTION III - UNIQUE OR NOVEL FEATURES OF THE TECHNOLOGY AND THE RESULTS (OR BENEFITS) OF ITS APPLICATION (Enter as appropriate A. - Novel or unique features; B. - Development or conceptual problems; C. - Operating characteristics, test data; D. - Analysis of capabilities; E. - Source of error; and F. - Advantages/shortcomings):

A. Portable, inexpensive, and specific detector for HCl vapor. Type of data display determined by the microbalance used for weighing mass of HCl absorbed.

B. Problem areas which can occur: a. uniform coating on substrate. b. multiple nitrogens per molecule. c. refurbishing saturated detector.

C. Operating characteristics, test data--See attached sheet.

D. This detector has a useful application in the monitoring of HCl vapor ? environmental and health problem areas.

E. Errors are usually dictated by microbalance used. Water vapor will give a response, but then returns to normal reading much more rapidly than the HCl does.

SIGNATURE OF INNOVATOR (S): Gary L. Workman

DATE: 10-10-75

APPENDIX D

Amines are being examined for use as coating material on quartz crystal microbalances for the detection of HCl (Hydrogen Chloride) in the atmosphere. The reaction between amines and HCl in the formation of the hydrogen chloride addition product:

$$\text{(primary amine)} \quad RNH_2 + HCl \longrightarrow RNH_3Cl$$

$$\text{(secondary amine)} \quad R_2NH + HCl \longrightarrow R_2NH_2Cl$$

$$\text{(tertiary amine)} \quad R_3N + HCl \longrightarrow R_3NHCl$$

Amines are classified as primary, secondary, or tertiary according to the number of groups attached to the nitrogen atom. These groups will be organic, that is they will consist of a carbon compounds either chains, rings, or a combination. The important point being that one carbon atom in the group must be bonded to the nitrogen. The carbon atom is sometimes called the amine carbon and must have no other substituent except carbon or hydrogen. The amine is primary if one group is attached to the carbon atom, secondary for two groups and tertiary for three. The remaining atoms bonded to the nitrogen atom in the case of primary and secondary amines will be hydrogen.

One important property of amines is that they are basic. A base can be defined in a number of ways. Amines will generally qualify in each category. One definition of a base is that it is a proton (Hydrogen ion, H^+) acceptor. (Bronsted-Lowery). Bases in aqueous solution (Arrhenius) will react with water

to produce hydroxide ion (OH-). Finally according to G. N. Lewis a base is an electron pair donor. As was previously stated most amines fit all three definitions:

(Proton acceptor) $RNH_2 + H^+ \longrightarrow RNH_3^+$

(Reaction with water) $RNH_2 + H_2O \longrightarrow RNH_3^+ + OH^-$

(Lewis Base) $M^{+n} + xRNH_2 \longrightarrow [M(RNH_2)_x]^{+n}$

Bases are also classified as strong or weak depending on whether they react completely with the solvent. For example most amines are weak bases especially in water:

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

This reaction does not go to completion. There is some unreacted (or undissociated) amine (RNH_2) in the solution. The extent of the reaction can be determined by the value of the base dissociation constant, K_b , which for the above reaction would be:

$$\frac{[RNH_3^+] \quad [OH^-]}{[RNH_2]} = K_b \quad .$$

Brackets [] indicates consentration of the species in moles per liter of solution. Amole is $6.02X\ 10^{23}$ molecules, atoms, or ions. The dissociation constant is an experimentally determined figure that is a property of the system i.e. the solvent and the particular base. K_b for a particular system generally varies only with temperature and is indicative of whether the reaction proceeds to completion. A large K_b indicates a strong base.

It is probably useful at this point to discuss acids since the reaction between amines and HCl is an acid-base reaction. The acid definitions are quite analogous to those for bases. The Bronsted-Lowery therory defines an acid as a proton (H^+) donor. Arrhenius defines a acid as any species that will produce hydronium ions in aqueous solution. A Lewis acid is an electron pair acceptor. The reaction product resulting from the reaction of an acid and a base may be acidic, basic, or neutral depending on the reactants. When a strong acid reacts with a strong base the product will be neutral (that is it won't fit the definition for acids or bases). When a strong acid reacts with a weak base, which is essentially the situation in the reaction between amines and HCl, the product will be acidic, that is amine-hydrochlorides are generally slightly acidic materials.

It could be possible to analyze for chloride in the determination of HCl. One of the problems associated with this approach is that HCl is probably not the only chloride containing material in rocket exhaust. Whereas HCl is likely to be the principal protonic acid present. Therefore the use of amines to react HCl to form the amine hydrochloride is the approach of choice.

There are many amines available, however, a consideration of what is desirable in coating material for QCM's will narrow the field considerably. Let us go over some of the considerations:

First of all the compound must react with HCl in a known

and preferably quantitative manner. This requirement can be met by most amines. The reaction with HCl must result in a mass change on the QCM. Again most amines would do this. The coating material should not be water soluble or hydroscopic, that is pick up water from the atomsphere, because it is quite probable that it will be desirable to analyze for HCl in humid climates. Now these requirements are quite restrictive because many amines are both water soluble and hydroscopic. The amine of choice should probably be a solid for good coating characterictics. The material should be specific for HCl. This is the most restrictive condition of all. Triphenyl amine, $(C_6H_5)_3N$, appears to be a favorable choice, and has been extensively tested for this purpose. (NASA TMX-64984 Dec. 1975) It is a tertiary amine molecular weight 245.31, melting point 126.4° C. boiling point 365° C. It is insoluble in water and therefore not hydroscopic. It is a weak base, $K_b = 6.3 \times 10^{-10}$ in anhydrous acetic acid, the hydrochloride melts at 214° C. The fact that triphenylamine is a very weak base is mixed blessing in that strong bases will, of course, react readily with HCl. However they will also react with any other acidic material present, for example carbon dioxide. Triphenylamine should be rather specific for a relatively strong protonic acid such as HCl. There is no readily available thermodynamic information on the reaction between triphenylamine and HCl. One of the principal derivatives listed for use in identification

of triphenylamine is the hydrochloride addition product we have been considering.

The reaction product between HCl and triphenylamine, triphenylaminehydrochloride, is a solid compound melting at 214° C. One would normally expect this compound to be fairly stable. Howeve-, we have found no specific experimental data to support this assumption. The expected reaction between HCl and triphenyl amine is:.

$$(C_6H_5)_3\ N_{(s)} + HCl_{(g)} \rightleftharpoons (C_6H_5)_3\ NHCl_{(s)}$$

If the reverse reaction, that is the decomposition of the triphenylaminehydrochloride, occurs subsquent to its formation, then one would observe a mass gain followed by a return to the initial mass. One could explain such behavior if the reaction is quite reversible. Once the HCl exposure is ended then the absence of HCl could cause the decomposition to occur.

Another reaction resulting in an initial mass gain followed by a mass loss could be the hydrolysis of the newly formed triphenylaminehydrochloride:

$$(C_6H_5)_3\ NHCl_{(s)} + H_2O_{(\ell)} \rightleftharpoons (C_6H_5)_3\ NHOH_{(s)} + HCl_{(g)}$$

This reaction would result in a mass loss but the loss would not amount to a return to the initial mass.